
Superfund



USEPA CONTRACT LABORATORY PROGRAM

STATEMENT OF WORK FOR INORGANICS ANALYSIS MULTI-MEDIA, MULTI-CONCENTRATION

SOW No. 788

Attachment A

USEPA CONTRACT LABORATORY PROGRAM

STATEMENT OF WORK

FOR

INORGANICS ANALYSIS

Multi-Media

Multi-Concentration

SOW No. 788

U.S. Environmental Protection Agency
Region 5, Library (PL-12J)
77 West Jackson Boulevard, 12th Floor
Chicago, IL 60604-3590

STATEMENT OF WORK

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EXHIBIT A

SUMMARY OF REQUIREMENTS

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SECTION I

GENERAL REQUIREMENTS

The Contractor shall employ procedures specified in this Statement of Work (SOW) in the preparation and analysis of aqueous (water) and solid (soil/sediment) samples for the presence and quantitation of 23 indicated elements and cyanide.

The Contractor shall use proven instruments and techniques to identify and measure the elements and inorganic species presented in the Target Analyte List (Exhibit C). The Contractor shall perform sample preparation and analysis procedures as prescribed in Exhibit D, meeting specified sample preservation and holding time requirements.

The Contractor shall adhere to the quality assurance/quality control protocol specified in Exhibit E for all samples analyzed under this contract.

Following sample analysis, the Contractor shall perform data reduction and shall report analytical activities, sample data, and quality control documentation as designated in Exhibit B. Specifications for reporting data in computer-readable format appear in Exhibit H.

Exhibit F contains chain-of-custody and document control requirements which the Contractor must follow in processing samples and specifies requirements for written laboratory standard operating procedures.

To ensure proper understanding of language utilized in this contract, Exhibit G contains a glossary of terms. When a term is used in the text without explanation, the glossary meaning shall be applicable. Glossary definitions do not replace or take precedence over specific information included in the SOW text.

The samples to be analyzed by the Contractor are from known or suspected hazardous waste sites and, potentially, may contain hazardous inorganic and/or organic materials at high concentration levels. The Contractor should be aware of the potential hazards associated with the handling and analyses of these samples. It is the Contractor's responsibility to take all necessary measures to ensure the health and safety of its employees.

SECTION II
SPECIFIC REQUIREMENTS

A. For each sample, the Contractor shall perform the following tasks:

Task I: Receive and Prepare Hazardous Waste Samples.

1. The Contractor shall receive and handle samples under the chain-of-custody and sample documentation procedures described in Exhibit F. A sample consists of all components, perhaps more than one phase, contained inside appropriate receptacles. More than one container may be used for a single sample; individual containers may contain preservatives for different analysis portions. Containers may be glass or plastic.
2. The Contractor shall provide the required analytical expertise and instrumentation for analyses of Target Analyte List (TAL) elements and cyanide equal to or lower than the detection limits specified in Exhibit C. In Exhibit D, EPA provides the Contractor with the specific sample preparation techniques for water and soil/sediment samples and the analytical procedures which must be used. A schematic flow chart depicting the complete low level-medium level inorganics analytical scheme is presented in Section I of Exhibit D.
3. The Contractor shall prepare and analyze samples within the maximum holding time specified in Section II of Exhibit D even if these times are less than the maximum data submission time allowed in this contract.
4. The Contractor is advised that the samples received under this contract are usually from known or suspected hazardous waste sites and may contain high (greater than 15%) levels of organic and inorganic materials of a potentially hazardous nature and of unknown structure and concentration, and should be handled throughout the analysis with appropriate caution. It is the Contractor's responsibility to take all necessary measures to ensure laboratory safety.

Task II: Analyze Samples for Identity and Quantitation of Specific Inorganic Constituents.

1. For each sample received, the Contractor may be required to perform the analyses described in paragraphs 2., 3. and 4., following. The documentation that accompanies the sample(s) to the Contractor facility shall indicate specific analytical requirements for that sample or set of samples.
2. Exhibit D specifies the analytical procedures that must be used. Exhibit D contains instructions and references for preparation of samples containing low-to-medium concentrations of inorganics for ICP analysis; flame, graphite furnace and cold vapor AA analysis;

and cyanide analysis. The identification and quantitation of analytes other than cyanide shall be accomplished using the ICP or AA methods specified in Exhibit D, whichever method will achieve the Contract Required Detection Limit (CRDL) in Exhibit C. Cyanide shall be analyzed by the individual procedures specified in Exhibit D.

3. All samples must initially be run undiluted (i.e., final product of sample preparation procedure). When an analyte concentration exceeds the calibrated or linear range, appropriate dilution (but not below the CRDL) and reanalysis of the prepared sample is required, as specified in Exhibit D.
4. For the purpose of this contract, a full sample analysis is defined as analysis for all of the TAL constituents identified in Exhibit C in accordance with the methods in Exhibit D and performance of related QA/QC as specified in Exhibit E. Duplicate sample, laboratory control sample, and spike sample analyses shall each be considered a separate full sample analysis. All other QA/QC requirements are considered an inherent part of this contract Statement of Work and are included in the contract sample unit price.

Task III: Perform Required Quality Assurance/Quality Control Procedures

1. All specific QA/QC procedures prescribed in Exhibit E shall be strictly adhered to by the Contractor. Records documenting the use of the protocol shall be maintained in accordance with the document control procedures prescribed in Exhibit F, and shall be reported in accordance with Exhibit B requirements.
 2. The Contractor shall establish and use on a continuing basis QA/QC procedures including the daily or (as required) more frequent use of standard reference solutions from EPA, the National Bureau of Standards or secondary standards traceable thereto, where available at appropriate concentrations (i.e., standard solutions designed to ensure that operating parameters of equipment and procedures, from sample receipt through identification and quantitation, produce reliable data). Exhibit E specifies the QA/QC procedures required.
 3. Additional quality assurance and quality control shall be required on a quarterly basis in the form of Performance Evaluation Samples submitted by EPA for Contractor analysis, and in the form of verification of instrument parameters, as described in Exhibit E.
- B. EPA has provided to the Contractor formats for the reporting of data (Exhibits B and H). The Contractor shall be responsible for completing and returning analysis data sheets and submitting computer-readable data on floppy diskette in the format specified in this SOW and within the time specified in the Contract Performance/Delivery Schedule.

1. Use of formats other than those designated by EPA will be deemed as noncompliance. Such data are unacceptable. Resubmission in the specified format at no additional cost to the government will be required.
 2. Computer generated forms may be submitted in the hardcopy data package(s) provided that the forms are in EXACT EPA FORMAT. This means that the order of data elements is the same as on each EPA required form, including form numbers and titles, page numbers and header information, columns and lines.
 3. The data reported by the Contractor on the hardcopy data forms and the associated computer-readable data submitted by the Contractor must contain identical information. If during government inspection discrepancies are found, the Contractor shall be required to resubmit either or both sets of data at no additional cost to the government.
- C. The Contractor shall provide analytical equipment and technical expertise for this contract as specified following:
1. Inductively coupled plasma (ICP) emission spectrometer with the capability to analyze metals sequentially or simultaneously.
 2. Atomic absorption (AA) spectrometer equipped with graphite furnace, flame, and cold vapor AA (or a specific mercury analyzer) analysis capabilities.
 3. Analytical equipment/apparatus for analysis of cyanide as described in Exhibit D.
- D. The Contractor shall have an IBM or IBM-compatible mini-computer or PC capable of recording required sample data on 5.25 inch floppy double-sided double-density 360 K-byte or 1.2 M-byte diskettes, in ASCII text file format and in accordance with the file, record and field specifications listed in Exhibit H.
- E. The minimum functional requirements necessary to meet the terms and conditions of this contract are listed in items 1-7 below. The Contractor shall designate and utilize qualified key personnel to perform these functions. The EPA reserves the right to review personnel qualifications and experience. See Section III, Detailed Technical & Management Requirements.
1. Laboratory Supervisor
 2. ICP Spectroscopist
 3. ICP Operator
 4. Atomic Absorption (AA) Operator
 5. Inorganic Sample Preparation Specialist
 6. Classical Techniques (Cyanide) Analyst
 7. Inorganic Chemist (Backup)

- F. The Contractor shall respond in a timely manner to requests from data recipients for additional information or explanations that result from the Government's inspection activities.
- G. The Contractor is required to retain unused sample volume and used sample containers for a period of 60 days after data submission. From time of receipt until analysis, the Contractor shall maintain soil/sediment samples stored at 4°C ($\pm 2^{\circ}\text{C}$).
- H. The Contractor shall adhere to chain-of-custody and document control procedures described in Exhibit F. Documentation, as described therein, shall be required to show that all procedures are being strictly followed. This documentation shall be reported in the Complete Case File Purge (see Exhibit B).
- I. Sample shipments to the Contractor's facility will be scheduled and coordinated by the EPA CLP Sample Management Office (SMO), acting on behalf of the Project Officer. The Contractor shall communicate with SMO personnel by telephone as necessary throughout the process of sample scheduling, shipment, analysis and data reporting, to ensure that samples are properly processed.

If there are problems with the samples (e.g., mixed media, containers broken or leaking) or sample documentation/paperwork (e.g., Traffic Reports not with shipment, or sample and Traffic Report numbers do not correspond) the Contractor shall immediately contact SMO for resolution. The Contractor shall immediately notify SMO regarding any problems and laboratory conditions that affect the timeliness of analyses and data reporting. In particular, the Contractor shall notify SMO personnel in advance regarding sample data that will be delivered late and shall specify the estimated delivery date.

- J. Sample analyses will be scheduled by groups of samples, each defined as a Case and identified by a unique EPA Case number assigned by SMO. A Case signifies a group of samples collected at one site or geographical area over a finite time period, and will include one or more field samples with associated blanks. Samples may be shipped to the Contractor in a single shipment or multiple shipments over a period of time, depending on the size of the Case. A Case consists of one or more Sample Delivery Group(s). A Sample Delivery Group (SDG) is defined by the following, whichever is most frequent:

- o each Case of field samples received, OR
- o each 20 field samples within a Case, OR
- o each 14 calendar day period during which field samples in a Case are received (said period beginning with the receipt of the first sample in the Sample Delivery Group).

Samples may be assigned to Sample Delivery Groups by matrix (i.e., all soils in one SDG, all waters in another), at the discretion of the laboratory. Such assignment must be made at the time the samples are received, and may not be made retroactively.

Data for all samples in a Sample Delivery Group must be submitted together (in one package) in the order specified in Exhibit B. The Sample Delivery Group number is the EPA sample number of the first sample received in the SDG. When several samples are received together in the first SDG shipment, the SDG number is the lowest sample number (considering both alpha and numeric designations) in the first group of samples received under the SDG. The SDG number is reported on all data reporting forms. The SDG Receipt Date is the day that the last sample in the SDG is received.

The Contractor is responsible for identifying each Sample Delivery Group as samples are received, through proper sample documentation (see Exhibit B) and communication with SMO personnel.

- K. Each sample received by the Contractor will be labeled with an EPA sample number, and accompanied by a Traffic Report form bearing the sample number and descriptive information regarding the sample. The Contractor shall complete and sign the Traffic Report, recording the date of sample receipt and sample condition on receipt for each sample container. The Contractor must also follow the instructions given on the Traffic Report in choosing the QC samples when such information is provided.

The Contractor shall submit signed copies of Traffic Reports for all samples in a Sample Delivery Group to SMO within 3 calendar days following receipt of the last sample in the Sample Delivery Group. Traffic Reports shall be submitted in Sample Delivery Group sets (i.e., all Traffic Reports for a Sample Delivery Group shall be clipped together) with an SDG Cover Sheet containing information regarding the Sample Delivery Group, as specified in Exhibit B.

- L. EPA Case numbers (including SDG numbers) and EPA sample numbers shall be used by the Contractor in identifying samples received under this contract both verbally and in reports/correspondence.
- M. Samples will routinely be shipped directly to the Contractor through a delivery service. The Contractor shall be available to receive sample shipments at any time the delivery service is operating, including Saturdays and holidays. As necessary, the Contractor shall be responsible for any handling or processing required for the receipt of sample shipments, including pick-up of samples at the nearest servicing airport, bus station or other carrier service within the Contractor's geographical area.
- N. The Contractor shall accept all samples scheduled by SMO, provided that the total number of samples received in any calendar month does not exceed the monthly limitation expressed in the contract. Should the Contractor elect to accept additional samples, the Contractor shall remain bound by all contract requirements for analysis of those samples accepted.

SECTION III

DETAILED TECHNICAL & MANAGEMENT REQUIREMENTS

As cited in Section II, Task III, the Contractor shall have the following technical and management capabilities:

A. TECHNICAL CAPABILITY

1. Technical Functions

a. Inorganics Laboratory Supervisor

(1) Responsible for all technical efforts of the Inorganics Laboratory to meet all terms and conditions of the contract.

(2) Qualifications

(a) Education:

Minimum of Bachelor's degree in chemistry or any scientific/engineering discipline.

(b) Experience:

Minimum of three years of laboratory experience, including at least one year in a supervisory position.

b. ICP Spectroscopist Qualifications

(1) Education:

- o Minimum of Bachelor's degree in chemistry or any scientific/engineering discipline.
- o Specialized training in ICP Spectroscopy.

(2) Experience:

Minimum of two years of applied experience with ICP analysis of environmental samples.

c. ICP Operator Qualifications

(1) Education:

Minimum of Bachelor's degree in chemistry or any scientific/engineering discipline.

(2) Experience:

Minimum of one year of experience in operating and maintaining ICP instrumentation, in conjunction with the educational requirement; or, in lieu of educational requirement, three additional years of experience in operating and maintaining ICP instrumentation.

d. Atomic Absorption (AA) Operator Qualifications

(1) Education:

Minimum of Bachelor's degree in chemistry or any scientific/engineering discipline.

(2) Experience:

Minimum of one year of experience in operating and maintaining AA instrumentation for each of the following AA techniques: (a) flame (if flame will be used), (b) graphite furnace, and (c) cold vapor, in conjunction with the educational requirement; or, in lieu of educational requirement, three additional years of experience in operating and maintaining AA instrumentation, including flame, graphite furnace, and cold vapor techniques.

e. Inorganic Sample Preparation Specialist Qualifications

(1) Education:

Minimum of high school diploma and a college level course in general chemistry or equivalent.

— (2) Experience:

Minimum of six months of experience in an analytical laboratory.

f. Classical Techniques (Cyanide) Analyst Qualifications

(1) Education:

Minimum of Bachelor's degree in chemistry or any scientific/engineering discipline.

(2) Experience:

Minimum of six months of experience with classical chemistry laboratory procedures, in conjunction with the educational qualifications; or, in lieu of educational requirement, two years of additional equivalent experience.

g. Technical Staff Redundancy

In order to ensure continuous operations to accomplish the required work as specified by EPA contract, the bidder shall have a minimum of one (1) chemist available at all times as a back-up technical person with the following qualifications.

(1) Education:

Minimum of Bachelor's degree in chemistry or any scientific/engineering discipline.

(2) Experience:

Minimum of one year of experience in each of the following areas -

- o ICP operation and maintenance
- o AA operation and maintenance
- o Classical chemistry analytical procedures
- o Sample preparation for inorganics analysis

2. Facilities

The adequacy of the facilities and equipment is of equal importance for the technical staff to accomplish the required work as specified by the EPA contract.

a. Sample Receipt Area

Adequate, contamination-free, well ventilated work space provided with chemical resistant bench top for receipt and safe handling of EPA samples.

b. Storage Area

Sufficient refrigerator space to maintain unused EPA sample volume for 60 days after data submission. Samples and standards must be stored separately.

c. Sample Preparation Area

Adequate, contamination-free, well-ventilated work space provided with:

- (1) Benches with chemical resistant tops.
- (2) Exhaust hoods. Note: Standards must be prepared in a glove box or isolated area.

(3) Source of distilled or demineralized organic-free water.

(4) Analytical balance(s) located away from draft and rapid change in temperature.

3. Instrumentation

At a minimum, the Contractor shall have the following instruments operative at the time of the Preaward Site Evaluation and committed for the full duration of the contract.

a. (1) 100 Samples/Month Capacity Requirements

Fraction	No. of Instrument(s)	Type of Instrument
ICP Metals	1	ICP Emission Spectrophotometer
GFAA Metals	1	Atomic Absorption Spectrophotometer with Graphite Furnace Atomizer
Mercury	1	Mercury Cold Vapor AA Analyzer or AA instrument modified for Cold Vapor Analysis
Cyanide	6 distillation units + 1 photometer	See Cyanide Methods, Statement of Work Exhibit D, Section IV, Part E

(2) Secondary Instrument Requirements for 100 Samples/Month Capacity

The Contractor shall have the following instruments available (operational) at all times as a back-up system:

<u>Quantity</u>	<u>Instruments</u>
one	Graphite Furnace AA
one	Mercury Cold Vapor AA System

These instruments must be included in the bidder's inventory of equipment. In addition, the Contractor shall have an in-house stock of instrument parts and circuit boards to ensure continuous operation to meet contract-specified holding and turnaround times.

b. (1) 200 Samples/Month Capacity Requirements

Fraction	No. of Instrument(s)	Type of Instrument
ICP Metals	1	ICP Emission Spectrophotometer
GFAA Metals	2	Atomic Absorption Spectrophotometer with Graphite Furnace Atomizer
Mercury	2	Mercury Cold Vapor AA Analyzer or AA instrument modified for Cold Vapor Analysis
Cyanide	12 distillation units + 1 photometer	See Cyanide Methods, Statement of Work Exhibit D, Section IV, Part E

(2) There are no Secondary Instrument Requirements for 200 Samples/Month Capacity.

c. **Secondary Instrument Requirements for 300 or Greater Samples/Month Capacity**

The Contractor shall have the following instruments available (operational) at all times as a back-up system:

<u>Quantity</u>	<u>Instruments</u>
one	ICP Emission Spectrophotometer
one	Graphite Furnace AA

These instruments must be included in the bidder's inventory of equipment. In addition, the Contractor shall have an in-house stock of instrument parts and circuit boards to ensure continuous operation to meet contract-specified holding and turnaround times.

d. **Instrument Specifications**

Further information on instrument specifications and required ancillary equipment may be found in this Exhibit and other Exhibits in this Statement of Work.

4. **Data Handling and Packaging**

The Contractor shall be able to submit reports and data packages as specified in the Statement of Work Exhibit B. To complete this task, the Contractor shall be required to:

- a. Provide space, tables and copy machines to meet the contract requirements.
- b. Designate personnel.

B. **LABORATORY MANAGEMENT CAPABILITY**

The Contractor must have an organization with well-defined responsibilities for each individual in the management system to ensure sufficient resources for EPA contract(s) and to maintain a successful operation. To establish this capability, the Contractor shall designate personnel to carry out the following responsibilities for the EPA contract. Functions include, but are not limited to, the following:

1. **Technical Staff**

Responsible for all technical efforts for the EPA contract.

2. Project Manager

Responsible for overall aspects of EPA contract(s) (from sample receipt to through data delivery) and shall be the primary contact for EPA Headquarters Project Officer and Regional Deputy Project Officers.

3. Sample Custodian

Responsible for receiving the EPA samples (logging, handling and storage).

4. Quality Assurance Officer

Responsible for overseeing the quality assurance aspects of the data and reporting directly to upper management.

5. Data Reporting and Delivery Officer

Responsible for all aspects of data deliverables: organization, packaging, copying, and delivery.

EXHIBIT B

REPORTING AND DELIVERABLES REQUIREMENTS

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SECTION I

CONTRACT REPORTS/DELIVERABLES DISTRIBUTION

The following table reiterates the Contract reporting and deliverables requirements specified in the Contract Schedule and specifies the distribution that is required for each deliverable. NOTE: Specific recipient names and addresses are subject to change during the term of the contract. The Project Officer will notify the Contractor in writing of such changes when they occur.

Item	Copies	Schedule	<u>Distribution</u>		
			(1)	(2)	(4)
*A. Contract Start-Up Plan	2	7 days after contract receipt.	X	X	
B. Updated SOPs	1	120 days after contract receipt.	X		X

Item	No. Copies	Delivery Schedule	(3)	<u>Distribution</u>		
				(4)	(5)	(6)
C. Sample Traffic Reports	1	3 days after receipt of last sample in Sample Delivery Group (SDG)**	X			
***D. Sample Data Package	3	35 days after receipt of last sample in SDG	X	X	X	
***E. Data in Computer-Readable Form	1	35 days after receipt of last sample in SDG	X			
F. Results of Inter-comparison Study/PE Sample Analysis	2	35 days after receipt of last sample in SDG	X	X		
G. Compilation of Complete Case File Purge	1	7 days after data submission		N/A	--	
H. Complete Case File Purge	1	180 days after data submission or 7 days from receipt of written request by PO or SMO				X

Item	No. Copies	Delivery Schedule	Distribution			
			(3)	(4)	(5)	(6)
**I. Quarterly Verification of Instrument Parameters	2	Quarterly: 15th day of January, April July, October	X	X		

Distribution:

- (1) Project Officer (PO)
- (2) Contract Officer (CO)
- (3) Sample Management Office (SMO)
- (4) EMSL-LV
- (5) Region-Client
- (6) NEIC

* Contractor must be prepared to receive samples within 30 days of Contract award. NOTE: EPA can't guarantee exact adherence to start-up plan that is agreed upon by PO and Contractor, but will attempt to meet it as close as possible.

** Also required in each Sample Data Package.

*** Concurrent delivery of these items to all recipients is required.

**** Sample Delivery Group (SDG) is a group of samples within a Case, received over a period of 14 days or less and not exceeding 20 samples. Data for all samples in the SDG are due concurrently. (See SOW Exhibit A, paragraph J., for further description).

NOTE: As specified in the Contract Schedule (Government Furnished Supplies and Materials), unless otherwise instructed by the CLP Sample Management Office, the Contractor shall dispose of unused sample volume and used sample bottles/containers no earlier than sixty (60) days following submission of analytical data.

Distribution Addresses:

- (1) USEPA Analytical Operations Branch (WH-548A)
401 M Street, SW
Washington, DC 20460
ATTN: (Project Officer's Name)
- (2) USEPA Contracts Management Division (MD-33)
Alexander Drive
Research Triangle Park, NC 27711
ATTN: (Contract Officer's Name)

- (3) USEPA Contract Laboratory Program (CLP)
Sample Management Office (SMO)
P. O. Box 818
Alexandria, VA 22313

For overnight delivery service, use street address:

209 N. Madison Street, 2nd Floor
Alexandria, VA 22314

- (4) USEPA Environmental Monitoring
Systems Laboratory (EMSL-LV)
P. O. Box 93478
Las Vegas, NV 89193-3478
ATTN: Data Audit Staff

For overnight delivery service, use street address:

944 E. Harmon, Executive Center
Las Vegas, NV 89109
ATTN: Data Audit Staff

- (5) USEPA REGIONS:

The CLP Sample Management Office, acting on behalf of the Project Officer, will provide the Contractor with the list of addressees for the ten EPA Regions. SMO will provide the Contractor with updated Regional address/name lists as necessary throughout the period of the contract and identify other client recipients on a case-by-case basis.

- (6) NEIC, Contractor Evidence Audit Team
2600 West Colfax, Suite C310
Lakewood, Colorado 80215

SECTION II

REPORT DESCRIPTIONS AND ORDER OF DATA DELIVERABLES

The Contractor laboratory shall provide reports and other deliverables as specified in the Contract Performance/Delivery Schedule (see Contract Schedule, Section F). The required content and form of each deliverable is described in this Exhibit.

All reports and documentation MUST BE:

- o Legible,
- o Clearly labeled and completed in accordance with instructions in this Exhibit,
- o Arranged in the order specified in this Section,
- o Paginated, and
- o Single-sided.

If submitted documentation does not conform to the above criteria, the Contractor will be required to resubmit such documentation with deficiency(ies) corrected, at no additional cost to the government.

Whenever the Contractor is required to submit or resubmit data as a result of an on-site laboratory evaluation or through a PO/DPO action, the data must be clearly marked as ADDITIONAL DATA and must be sent to all three contractual data recipients (SMO, EMSL-LV, and Region). A cover letter shall be included which describes what data is being delivered, to which EPA Case(s) the data pertains, and who requested the data.

Whenever the Contractor is required to submit or resubmit data as a result of Contract Compliance Screening (CCS) review by SMO, the data must be sent to all three contractual data recipients (SMO, EMSL/LV and Region), and in all three instances must be accompanied by a color-coded COVER SHEET (Laboratory Response To Results of Contract Compliance Screening) provided by SMO.

Section IV of this Exhibit contains the required Inorganic Analysis Data Reporting Forms in Agency-specified formats; Section III of this Exhibit contains instructions to the Contractor for properly completing all data reporting forms to provide the Agency with all required data. Data elements and field descriptors for reporting data in computer-readable format are contained in Exhibit H.

Descriptions of the requirements for each deliverable item cited in the Contract Performance/Delivery Schedule (see Contract Schedule, Section F) are specified in parts A-G of this Section. Items submitted concurrently must be arranged in the order listed. Additionally, the components of each item must be arranged in the order presented herein when the item is submitted.

A. Contract Start-Up Plan

The Contractor shall submit a contract start-up plan for EPA approval as specified in the Contract Performance/Delivery Schedule. The plan shall set forth the Contractor's proposed schedule for receiving samples starting with the 30th calendar day after award and ending with the date the Contractor is capable of receiving the full monthly sample allotment stipulated in the Contract. The Project Officer will review the contract start-up plan within 7 days of submission and will notify the Contractor of the plan's status.

NOTE: The Contractor shall be required to receive samples within 30 days of contract award. EPA can't guarantee exact adherence to start-up plan that is agreed upon by the PO and Contractor, but will attempt to meet it as close as possible.

B. Updated SOPs

The Contractor shall submit updated copies of all required Standard Operating Procedures (SOPs) that were submitted with the prebid Performance Evaluation sample results. The updated SOPs must address any and all issues of laboratory performance and operation identified through the review of the Performance Evaluation sample data and the evaluation of Bidder-Supplied Documentation.

The Contractor must supply SOPs for:

1. Sample receipt and logging.
2. Sample and extract storage.
3. Preventing sample contamination.
4. Security for laboratory and samples.
5. Traceability/Equivalency of standards.
6. Maintaining instrument records and logbooks.
7. Sample analysis and data control systems.
8. Glassware cleaning.
9. Technical and managerial review of laboratory operation and data package preparation.
10. Internal review of contractually-required quality assurance and quality control data for each individual data package.
11. Sample analysis, data handling and reporting.
12. Chain-of-custody.
13. Document control, including case file preparation.

C. Sample Traffic Reports

Original Sample Traffic Report page marked "Lab Copy for Return to SMO" with lab receipt information and signed in original Contractor signature, shall be submitted for each sample in the Sample Delivery Group.

Traffic Reports (TRs) shall be submitted in Sample Delivery Group (SDG) sets (i.e., TRs for all samples in an SDG shall be clipped together), with an SDG Cover Sheet attached.

The SDG Cover Sheet shall contain the following items:

- o Lab name
- o Contract number
- o Sample Analysis Price - full sample price from contract.
- o Case Number
- o List of EPA sample numbers of all samples in the SDG, identifying the first and last samples received, and their dates of receipt.

NOTE: When more than one sample is received in the first or last SDG shipment, the "first" sample received would be the lowest sample number (considering both alpha and numeric designations); the "last" sample received would be the highest sample number (considering both alpha and numeric designations).

In addition, each Traffic Report must be clearly marked with the SDG Number, the sample number of the first sample in the SDG (as described in the following paragraph). This information should be entered below the Lab Receipt Date on the TR.

The EPA sample number of the first sample received in the SDG is the SDG number. When several samples are received together in the first SDG shipment, the SDG number shall be the lowest sample number (considering both alpha and numeric designations) in the first group of samples received under the SDG. (The SDG number is also reported on all data reporting forms. See Section III, Form Instruction Guide.)

If samples are received at the laboratory with multi-sample Traffic Reports (TRs), all the samples on one multi-sample TR may not necessarily be in the same SDG. In this instance, the laboratory must make the appropriate number of photocopies of the TR, and submit one copy with each SDG cover sheet.

D. Sample Data Package

The sample data package shall include data for analysis of all samples in one Sample Delivery Group (SDG), including analytical (field) samples, reanalyses, blanks, spikes, duplicates, and laboratory control samples.

The sample data package must be complete before submission, must be consecutively paginated (starting with page number one and ending with the number of all pages in the package), and shall include the following:

1. Cover Page for the Inorganic Analyses Data Package, (COVER PAGE -- Inorganic Analyses Data Package), including: laboratory name; laboratory code; contract number; Case No.; Sample Delivery Group (SDG) No.; Statement of Work (SOW) number (appears on cover page of SOW); EPA sample numbers in alphanumeric order, showing EPA sample numbers cross-referenced with lab ID numbers; comments, describing in detail any problems encountered in processing the samples in the data package; and, completion of the statement on use of ICP background and interelement corrections for the samples.

The Cover Page shall contain the following statement, verbatim: "I certify that this data package is in compliance with the terms and conditions of the contract, both technically and for completeness, for other than the conditions detailed above. Release of the data contained in this hardcopy data package and in the computer-readable data submitted on floppy diskette has been authorized by the Laboratory Manager or the Manager's designee, as verified by the following signature." This statement shall be directly followed by the signature of the Laboratory Manager or his designee with a typed line below it containing the signers name and title, and the date of signature.

In addition, on a separate piece of paper, the Contractor must also include any problems encountered; both technical and administrative, the corrective action taken and resolution.

2. Sample Data

Sample data shall be submitted with the Inorganic Analysis Data Reporting Forms for all samples in the SDG, arranged in increasing alphanumeric EPA sample number order, followed by the QC analyses data, Quarterly Verification of Instrument Parameters forms, raw data, and copies of the digestion and distillation logs.

- a. Results -- Inorganic Analysis Data Sheet [FORM I - IN]

- Tabulated analytical results (identification and quantitation) of the specified analytes (Exhibit C). The validation and release of these results is authorized by a specific, signed statement on the Cover Page. If the Laboratory Manager cannot validate all data reported for each sample, he/she must provide a detailed description of the problems associated with the sample(s) on the Cover Page.

Appropriate concentration units must be specified and entered on Form I. The quantitative values shall be reported in units of micrograms per liter (ug/L) for aqueous samples and milligrams per kilogram (mg/kg) for solid samples. No other units are acceptable. Results for solid samples must be reported on a dry weight basis. Analytical results must be reported to two significant figures if the result value is less than 10; to three significant figures if the value is greater than or equal to 10. Results for percent solids must be reported to one decimal place. The preceding discussion concerning significant numbers applies to Form I only. For

other Forms, follow the instructions specific to those forms as contained in this exhibit.

b. Quality Control Data

- 1) Initial and Continuing Calibration Verification [FORM II (PART 1) - IN]
- 2) CRDL Standard for AA and Linear Range Analysis for ICP [FORM II (PART 2) - IN]
- 3) Blanks [FORM III - IN]
- 4) ICP Interference Check Sample [FORM IV - IN]
- 5) Spike Sample Recovery [FORM V (PART 1) - IN]
- 6) Post Digest Spike Sample Recovery [FORM V (PART 2) - IN]
- 7) Duplicates [FORM VI - IN]
- 8) Laboratory Control Sample [FORM VII - IN]
- 9) Standard Addition Results [FORM VIII - IN]
- 10) ICP Serial Dilutions [FORM IX - IN]
- 11) Preparation Log [Form XIII - IN]
- 12) Analysis Run Log [Form XIV - IN]

c. Quarterly Verification of Instrument Parameters

- 1) Instrument Detection Limits (Quarterly) [FORM X - IN]
- 2) ICP Interelement Correction Factors (Annually) [FORM XI (PART 1) - IN]
- 3) ICP Interelement Correction Factors (Annually) [FORM XI (PART 2) - IN]
- 4) ICP Linear Ranges (Quarterly) [FORM XII - IN]

(Note that copies of Quarterly Verification of Instrument Parameters forms for the current quarter must be submitted with each data package.)

d. Raw Data

For each reported value, the Contractor shall include in the data package all raw data used to obtain that value. This applies to all required QA/QC measurements, instrument standardization, as well as all sample analysis results. This statement does not apply to the Quarterly Verification of Instrument Parameters submitted as a part of each data package.

Raw data must contain all instrument readouts used for the sample results. Each exposure or instrumental reading must be provided, including those readouts that may fall below the IDL. All AA and ICP instruments must provide a legible hard copy of the direct real-time instrument readout (i.e., stripcharts, printer tapes, etc.). A photocopy of the instruments direct sequential readout must be included. A hardcopy of the instrument's direct instrument readout for cyanide must be included if the instrumentation has the capability.

The order of raw data in the data package shall be: ICP, Flame AA, Furnace AA, Mercury, and Cyanide. All raw data shall include concentration units for ICP and absorbances with concentration units for flame AA, furnace AA, Mercury and Cyanide. All flame and furnace AA data shall be grouped by element.

Raw data must be labeled with EPA sample number and appropriate codes, shown in Table 1 following, to unequivocally identify:

- 1) Calibration standards, including source and prep date.
- 2) Initial and continuing calibration blanks and preparation blanks.
- 3) Initial and continuing calibration verification standards, interference check samples, ICP serial dilution samples, CRDL Standard for ICP and AA, Laboratory Control Sample and Post Digestion Spike.
- 4) Diluted and undiluted samples (by EPA sample number) and all weights, dilutions and volumes used to obtain the reported values. (If the volumes, weights and dilutions are consistent for all samples in a given SDG, a general statement outlining these parameters is sufficient).
- 5) Duplicates.
- 6) Spikes (indicating standard solutions used, final spike concentrations, volumes involved). If spike information (source, concentration, volume) is consistent for a given SDG, a general statement outlining these parameters is sufficient.
- 7) Instrument used, any instrument adjustments, data corrections or other apparent anomalies on the measurement record, including all data voided or data not used to obtain reported values and a brief written explanation.
- 8) All information for furnace analysis clearly and sequentially identified on the raw data, including EPA sample number, sample and analytical spike data, percent recovery, coefficient of variation, full MSA data, MSA correlation coefficient, slope and intercepts of linear fit, final sample concentration (standard addition

concentration), and type of background correction used: BS for Smith-Heftje, BD for Deuterium Arc, or BZ for Zeeman.

9) Time and date of each analysis. Instrument run logs can be submitted if they contain this information. If the instrument does not automatically provide times of analysis, these must be manually entered on all raw data for initial and continuing calibration verification and blanks, as well as interference check samples and CRDL standard for ICP.

10) Integration times for AA analyses.

e. Digestion and Distillation Logs

Logs shall be submitted in the following order: digestion logs for ICP, flame AA, furnace AA and mercury preparations, followed by a copy of the distillation log for cyanide. These logs must include: (1) date, (2) sample weights and volumes, (3) sufficient information to unequivocally identify which QC samples (i.e., laboratory control sample, preparation blank) correspond to each batch digested, (4) comments describing any significant sample changes or reactions which occur during preparation, and (5) indication of pH <2 or >12, as applicable.

3. A legible copy of the Sample Traffic Reports submitted in Item A for all of the samples in the SDG. The Traffic Reports shall be arranged in increasing EPA Sample Number order, considering both alpha and numeric designations. A legible photocopy of the SDG cover sheet must also be submitted.

E. Data in Computer Readable Form

The Contractor shall provide a computer-readable copy of the data on data reporting Forms I-XIV for all samples in the Sample Delivery Group, as specified in the Contract Performance/Delivery Schedule. Computer-readable data deliverables shall be submitted on an IBM or IBM-compatible, 5.25 inch floppy double-sided, double density 360 K-byte or a high density 1.2 M-byte diskette or on an IBM or IBM-compatible, 3.5 inch double-sided, double density 720 K-byte or a high density 1.44 M-byte diskette. The data shall be recorded in ASCII, text file format, and shall adhere to the file, record and field specifications listed in Exhibit H, Data Dictionary and Format for Data Deliverables in Computer-Readable Format.

When submitted, floppy diskettes shall be packaged and shipped in such a manner that the diskette(s) cannot be bent or folded, and will not be exposed to extreme heat or cold or any type of electromagnetic radiation. The diskette(s) must be included in the same shipment as the hardcopy data and shall, at a minimum, be enclosed in a diskette mailer.

Table 1

Codes for Labelling Raw Data

Sample	XXXXXX
Duplicate	XXXXXXD
Matrix Spike	XXXXXXS
Serial Dilution	XXXXXXL
Analytical Spike	XXXXXXA
Post Digestion/Distillation Spike	XXXXXXA
MSA:	
Zero Addition	XXXXXX0
First Addition	XXXXXX1
Second Addition	XXXXXX2
Third Addition	XXXXXX3
Instrument Calibration Standards:	
ICP	S or S0 for blank standard
Atomic Absorption and Cyanide	S0, S10,...etc.
Initial Calibration Verification	ICV
Initial Calibration Blank	ICB
Continuing Calibration Verification	CCV
Continuing Calibration Blank	CCB
Interference Check Samples:	
Solution A	ICSA
Solution AB	ICSAB
CRDL Standard for AA	CRA
CRDL Standard for ICP	CRI
Laboratory Control Samples:	
Aqueous (Water)	LCSW
Solid (Soil/Sediment)	LCSS
Preparation Blank (Water)	PBW
Preparation Blank (Soil)	PBS
Linear Range Analysis Standard	LRS

Notes:

1. When an analytical spike or MSA is performed on samples other than field samples, the "A", "0", "1", "2" or "3" suffixes must be the last to be added to the EPA Sample Number. For instance, an analytical spike of a duplicate must be formatted "XXXXXXDA."
2. The numeric suffix that follows the "S" suffix for the standards indicates the true value of the concentration of the standard in ug/L.
3. ICP calibration standards usually consist of several analytes at different concentrations. Therefore, no numeric suffix can follow the ICP calibration standards unless all the analytes in the standard are prepared at the same concentrations. For instance, the blank for ICP must be formatted "S0."

4. The CRDL standard for AA is considered to be a calibration standard if it was a part of the calibration curve, thus it must be formatted like any other standard. The "CRA" format must be used if the CRDL standard for AA is not used to establish the calibration curve.

F. Results of Intercomparison/Performance Evaluation(PE) Sample Analyses

Tabulation of analytical results for Intercomparison/PE Sample analyses include all requirements specified in items D. and E., above.

G. Compilation of Complete Case File Purge

Within 7 days after data submission, the Contractor shall have compiled the Complete Case File Purge package described in item H., following.

H. Complete Case File Purge

The Complete Case File Purge package includes all laboratory records received or generated for a specific Case that have not been previously submitted to EPA as a deliverable. These items shall be submitted along with their Case File Document Inventory (see Exhibit F, paragraph 2.4 for description of document numbering and inventory procedure). These items include, but are not limited to: sample tags, custody records, sample tracking records, analysts logbook pages, bench sheets, instrument readout records, computer printouts, raw data summaries, instrument logbook pages (including instrument conditions), correspondence, and the document inventory.

Shipment of the Complete Case File Purge package by first class mail, overnight carrier, priority mail or equivalent is acceptable. Custody seals, which are provided by EPA, must be placed on shipping containers and a document inventory and transmittal letter included. The Contractor is not required to maintain any documents for a sample Case after submission of the Complete Case File Purge package; however, the Contractor should maintain a copy of the document inventory and transmittal letter.

I. Quarterly Verification of Instrument Parameters

The Contractor shall perform and report quarterly verification of instrument detection limits and linear range by methods specified in Exhibit E for each instrument used under this contract. For the ICP instrumentation and methods, the Contractor shall also report quarterly interelement correction factors (including method of determination), wavelengths used, and integration times. Quarterly Verification of Instrument Parameters forms for the current quarter shall be submitted in each Sample Delivery Group data package, using Forms X, XI and XII. Submission of Quarterly Verification of Instrument Parameters shall include the raw data used to determine those values reported.

SECTION III

FORM INSTRUCTION GUIDE

This section contains specific instructions for the completion of all required Inorganic Data Reporting Forms. This section is organized into the following Parts:

- A. General Information and Header Information
- B. Cover Page -- Inorganic Analyses Data Package [COVER PAGE - IN]
- C. Inorganic Analysis Data Sheet [FORM I - IN]
- D. Initial and Continuing Calibration Verification [FORM II (PART 1) - IN]
- E. CRDL Standard for AA and ICP [FORM II (PART 2) - IN]
- F. Blanks [FORM III - IN]
- G. ICP Interference Check Sample [FORM IV - IN]
- H. Spike Sample Recovery [FORM V (PART 1) - IN]
- I. Post Digest Spike Sample Recovery [FORM V (PART 2) - IN]
- J. Duplicates [FORM VI - IN]
- K. Laboratory Control Sample [FORM VII - IN]
- L. Standard Addition Results [FORM VIII - IN]
- M. ICP Serial Dilutions [FORM IX - IN]
- N. Instrument Detection Limits (Quarterly) [FORM X - IN]
- O. ICP Interelement Correction Factors (Annually) [FORM XI (PART 1) - IN]
- P. ICP Interelement Correction Factors (Annually) [FORM XI (PART 2) - IN]
- Q. ICP Linear Ranges (Quarterly) [FORM XII - IN]
- R. Preparation Log [Form XIII - IN]
- S. Analysis Run Log [Form XIV - IN]

A. General Information and Header Information

The data reporting forms presented of Section IV in this Exhibit have been designed in conjunction with the computer-readable data format specified in Exhibit H, Data Dictionary and Format for Data Deliverables in Computer-Readable Format. The specific length of each variable for computer-readable data transmission purposes is given in the Data Dictionary (Exhibit H). Information entered on these forms must not exceed the size of the field given on the form, including such laboratory-generated items as Lab Name and Lab Sample ID.

Note that on the hardcopy forms (see Section IV), the space provided for entries is greater in some instances than the length prescribed for the variable as written to diskette (see Exhibit H). Greater space is provided on the hardcopy forms for the sake of visual clarity.

Values must be reported on the hardcopy forms according to the individual form instructions in this Section. Each form submitted must be filled out completely for all analytes before proceeding to the next form of the same type. Multiple forms cannot be submitted in place of one form if the information on those forms can be submitted on one form.

All characters which appear on the data reporting forms presented in the contract (Exhibit B, Section IV) must be reproduced by the Contractor when submitting data, and the format of the forms submitted must be identical to that shown in the contract. No information may be added, deleted, or moved from its specified position without prior written approval of the EPA Project Officer. The names of the various fields and analytes (i.e., "Lab Code", "Aluminum") must appear as they do on the forms in the contract, including the options specified in the form (i.e., "Matrix (soil/water):" must appear, not just "Matrix").

All alphabetic entries made onto the forms by the Contractor must be in ALL UPPERCASE letters (i.e., "LOW", not "Low" or "low"). If an entry does not fill the entire blank space provided on the form, null characters must be used to remove the remaining underscores that comprise the blank line. (See Exhibit H for more detailed instructions.) However, do not remove the underscores or vertical bar characters that delineate "boxes" on the forms.

Six pieces of information are common to the header sections of each data reporting form. These are: Lab Name, Contract, Lab Code, Case No., SAS No., and SDG No. This information must be entered on every form and must match on all forms.

The "Lab Name" must be the name chosen by the Contractor to identify the laboratory. It may not exceed 25 characters.

The "Contract" is the number of the EPA contract under which the analyses were performed.

The "Lab Code" is an alphabetic abbreviation of up to 6 characters, assigned by EPA, to identify the laboratory and aid in data processing. This lab code shall be assigned by EPA at the time a contract is awarded, and must not be modified by the Contractor, except at the direction of EPA.

The "Case No." is the EPA-assigned Case number (to 5 spaces) associated with the sample, and reported on the Traffic Report.

The "SAS No." is the EPA-assigned number for analyses performed under Special Analytical Services. If samples are to be analyzed under SAS only, and reported on these forms, then enter SAS No. and leave Case No. blank. If samples are analyzed according to this SOW (Routine Analytical Services protocol) and have additional SAS requirements, list both Case No. and SAS No. on all forms. If the analyses have no SAS requirements, leave "SAS No." blank. (NOTE: Some samples in an SDG may have a SAS No., while others do not.)

The "SDG No." is the Sample Delivery Group (SDG) number. The SDG number is the EPA Sample Number of the first sample received in the SDG. When several samples are received together in the first SDG shipment, the SDG number must be the lowest sample number (considering both alpha and numeric designations) in the first group of samples received under the SDG.

The other information common to several of the forms is the "EPA Sample No.". This number appears either in the upper righthand corner of the form, or as the left column of a table summarizing data from a number of samples. When "EPA Sample No." is entered into the triple-spaced box in the upper righthand corner of a form, it must be centered on the middle line of the three lines that comprise the box.

All samples, matrix spikes and duplicates must be identified with an EPA Sample Number. For samples, matrix spikes and duplicates, the EPA Sample Number is the unique identifying number given in the Traffic Report that accompanied that sample.

In order to facilitate data assessment, the sample suffixes listed in Table 1 must be used.

Other pieces of information are common to many of the Data Reporting Forms. These include: Matrix and Level.

For "Matrix", enter "SOIL" for soil/sediment samples, and enter "WATER" for water samples. NOTE: The matrix must be spelled out. Abbreviations such as "S" or "W" must not be used.

For "Level", enter the determination of concentration level. Enter as "LOW" or "MED", not "L" or "M".

Note: All results must be transcribed to Forms II-XIV from the raw data to the specified number of decimal places that are described in Exhibit B and Exhibit H. The raw data result is to be rounded only when the number of figures in the raw data result exceeds the maximum number of

figures specified for that result entry for that form. If there are not enough figures in the raw data result to enter in the specified space for that result, then zeros must be used for decimal places to the specified number of reporting decimals for that result for a specific form. The following examples are provided:

<u>Raw Data Result</u>	<u>Specified Format</u>	<u>Correct Entry on Form</u>
95.99653	5.4 (to four decimal places)	95.9965
95.99653	5.3 (to three decimal places)	95.997
95.99653	5.2 (to two decimal places)	96.00
95.996	5.4 (to four decimal places)	95.9960
95.9	5.4 (to four decimal places)	95.9000

For rounding off numbers to the appropriate level of precision, observe the following common rules. If the figure following those to be retained is less than 5, drop it (round down). If the figure is greater than 5, drop it and increase the last digit to be retained by 1 (round up). If the figure following the last digit to be retained equals 5 and there are no digits to the right of the 5 or all digits to the right of the 5 equals zero, then round up if the digit to be retained is odd, or round down if that digit is even. See also Rounding Rules entry in Glossary (Exhibit G).

Before evaluating a number for being in control or out of control of a certain limit, the number evaluated must be rounded using EPA rounding rules to the significance reported for that limit. For instance, the control limit for an ICV is plus or minus 10% of the true value. A reported percent recovery value of 110.4 would be considered in control while a reported value of 110.6 would be considered out of control. In addition, a calculated value of 110.50 would be in control while a calculated value of 110.51 would be out of control.

B. Cover Page - Inorganic Analyses Data Package [COVER PAGE-IN]

This form is used to list all samples analyzed within a Sample Delivery Group, and to provide certain analytical information and general comments. It is also the document which is signed by the Laboratory Manager to authorize and release all data and deliverables associated with the SDG.

Complete the header information according to the instructions in Part A.

The "SOW No." is the EPA-designated number that indicates the Statement of Work (SOW) version under which analyses in the data package have been performed. The SOW No. appears on the cover of the contract Statement of Work. For samples analyzed using this SOW, enter "7/88" for SOW No.

Enter the EPA Sample No. (including spikes and duplicates) (to seven spaces) of every sample analyzed within the SDG. Spikes must contain an "S" suffix and duplicates a "D" suffix. These sample numbers must be listed on the form in ascending alphanumeric order. Thus, if MAB123 is the lowest (considering both alpha and numeric characters) EPA Sample No. within the SDG, it would be entered in the first EPA Sample No. field. Samples would be listed below it, in ascending sequence - MAB124, MAB125, MAC111, MA1111, MA1111D, etc.

A Lab Sample ID (to ten spaces) may be entered for each EPA Sample No. If a Lab Sample ID is entered, it must be entered identically (for each EPA Sample No.) on all associated data.

Enter "YES" or "NO" in answer to each of the two questions concerning ICP corrections. Each question must be explicitly answered with a "YES" or a "NO". The third question must be answered with a "YES" or "NO" if the answer to the second question is "YES". It should be left blank if the answer to the second question is "NO".

Under "Comments", enter any statements relevant to the analyses performed under the SDG as a whole.

Each Cover Page must be signed, in original, by the Laboratory Manager or the Manager's designee and dated, to authorize the release and verify the contents of all data and deliverables associated with an SDG.

C. Inorganic Analysis Data Sheet [FORM 1-IN]

This form is used to tabulate and report sample analysis results for target analytes (Exhibit C).

Complete the header information according to the instructions in Part A and as follows.

"Date Received" is the date (formatted MM/DD/YY) of sample receipt at the laboratory, as recorded on the Traffic Report, i.e., the Validated Time of Sample Receipt (VTSR).

"% Solids" is the percent of solids on a weight/weight basis in the sample as determined by drying the sample as specified in Exhibit D. Report percent solids to one decimal place (i.e., 5.3%). If the percent solids is not required because the sample is fully aqueous or less than 1% solids, then enter "0.0".

Enter the appropriate concentration units (UG/L for water or MG/KG dry weight for soil). Entering "MG/KG" means "mg/Kg dry weight" on this form.

Under the column labeled "Concentration", enter for each analyte either the value of the result (if the concentration is greater than or equal to the Instrument Detection Limit) or the Instrument Detection Limit for the analyte corrected for any dilutions (if the concentration is less than the Instrument Detection Limit).

Under the columns labeled "C", "Q", and "M", enter result qualifiers as identified below. If additional qualifiers are used, their explicit definitions must be included on the Cover Page in the Comments section.

FORM I-IN includes fields for three types of result qualifiers. These qualifiers must be completed as follows:

- o C (Concentration) qualifier -- Enter "B" if the reported value was obtained from a reading that was less than the Contract Required Detection Limit (CRDL) but greater than or equal to the Instrument Detection Limit (IDL). If the analyte was analyzed for but not detected, a "U" must be entered.
- o Q qualifier -- Specified entries and their meanings are as follows:
 - E - The reported value is estimated because of the presence of interference. An explanatory note must be included under Comments on the Cover Page (if the problem applies to all samples) or on the specific FORM I-IN (if it is an isolated problem).
 - M - Duplicate injection precision not met.
 - N - Spiked sample recovery not within control limits.
 - S - The reported value was determined by the Method of Standard Additions (MSA).
 - W - Post-digestion spike for Furnace AA analysis is out of control limits (85-115%), while sample absorbance is less than 50% of spike absorbance. (See Exhibit E.)
 - * - Duplicate analysis not within control limits.
 - + - Correlation coefficient for the MSA is less than 0.995.

Entering "S", "W", or "+" is mutually exclusive. No combination of these qualifiers can appear in the same field for an analyte.

- o M (Method) qualifier -- Enter:
 - "P" for ICP
 - "A" for Flame AA
 - "F" for Furnace AA
 - "CV" for Manual Cold Vapor AA
 - "AV" for Automated Cold Vapor AA
 - "AS" for Semi-Automated Spectrophotometric
 - "C" for Manual Spectrophotometric
 - "T" for Titrimetric
 - "NR" if the analyte is not required to be analyzed.

A brief physical description of the sample, both before and after digestion, must be reported in the fields for color (before and after), clarity (before and after), texture and artifacts. For water samples, report color and clarity. For soil samples, report color, texture and artifacts.

The following descriptive terms are recommended:

Color	-	red, blue, yellow, green, orange, violet, white, colorless, brown, grey, black
Clarity	-	clear, cloudy, opaque
Texture	-	fine (powdery), medium (sand), coarse (large crystals or rocks)

If artifacts are present, enter "YES" in the artifacts field and describe the artifacts in the Comments field. If artifacts are not present, leave this field blank.

Note any significant changes that occur during sample preparation (i.e., emulsion formation) in the Comments field. Enter any sample-specific comments concerning the analyte results in the Comments field.

D. Initial and Continuing Calibration Verification [FORM II(PART 1)-IN]

This form is used to report analyte recoveries from calibration solutions.

Complete the header information according to the instructions in Part A and as follows.

Enter the Initial Calibration Source (12 spaces maximum) and the Continuing Calibration Source (12 spaces maximum). Enter "EPA-LV" or "EPA-CI" to indicate EPA EMSL Las Vegas or Cincinnati, respectively, as the source of EPA standards. When additional EPA supplied solutions are prepared in the future, the Contractor must use the codes supplied with those solutions for identification. If other sources were used, enter sufficient information in the available 12 spaces to identify the manufacturer and the solution used.

Use additional FORMs II(PART 1)-IN if more calibration sources were used.

Under "Initial Calibration True", enter the value (in ug/L, to one decimal place) of the concentration of each analyte in the Initial Calibration Verification Solution.

Under "Initial Calibration Found", enter the most recent value (in ug/L, to two decimal places), of the concentration of each analyte measured in the Initial Calibration Verification Solution.

Under "Initial Calibration %R", enter the value (to one decimal place) of the percent recovery computed according to the following equation:

$$\%R = \frac{\text{Found(ICV)}}{\text{True(ICV)}} \times 100 \quad (2.1)$$

Where, True(ICV) is the true concentration of the analyte in the Initial Calibration Verification Solution and Found(ICV) is the found concentration of the analyte in the Initial Calibration Verification Solution.

The values used in equation 2.1 for True(ICV) and Found(ICV) must be exactly those reported on this form.

Under "Continuing Calibration True", enter the value (in ug/L, to one decimal place) of the concentration of each analyte in the Continuing Calibration Verification Solution.

Under "Continuing Calibration Found", enter the value (in ug/L, to two decimal places) of the concentration of each analyte measured in the Continuing Calibration Verification Solution.

Note that the form contains two "Continuing Calibration Found" columns. The column to the left must contain values for the first Continuing Calibration Verification, and the column to the right must contain values for the second Continuing Calibration Verification. The column to the right should be left blank if no second Continuing Calibration Verification was performed.

If more than one FORM II(PART 1)-IN is required to report multiple Continuing Calibration Verifications, then the column to the left on the second form must contain values for the third Continuing Calibration Verification, the column to the right must contain values for the fourth Continuing Calibration Verification, and so on.

Under "Continuing Calibration %R", enter the value (to one decimal place) of the percent recovery computed according to the following equation:

$$\%R = \frac{\text{Found(CCV)}}{\text{True(CCV)}} \times 100 \quad (2.2)$$

where, True(CCV) is the true concentration of each analyte, and Found(CCV) is the found concentration of the analyte in the Continuing Calibration Verification Solution.

The values used in equation 2.2 for True(CCV) and Found(CCV) must be exactly those reported on this form.

Note that the form contains two "Continuing Calibration %R" columns. Entries to these columns must follow the sequence detailed above for entries to the "Continuing Calibration Found" columns.

Under "M", enter the method used or "NR", as explained in Part C.

If more than one wavelength is used to analyze an analyte, submit additional FORMs II(PART 1)-IN as appropriate.

The order of reporting ICVs and CCVs for each analyte must follow the temporal order in which the standards were run starting with the first Form IIA and moving from the left to the right continuing to the following Form IIA's as appropriate. For instance, the first ICV for all analytes must be reported on the first Form IIA. In a run where three CCVs were analyzed, the first CCV must be reported in the left CCV column on the first Form IIA and the second CCV must be reported in the right column of the same form. The third CCV must be reported in the left CCV column of the second Form IIA. On the second Form IIA, the ICV column and the right CCV column must be left empty in this example. In the previous example, if a second run for an analyte was needed, the ICV of that run must be reported on a third Form IIA and the CCVs follow in the same fashion as explained before. In the case where two wavelengths are used for an analyte, all ICV and CCV results of one wavelength from all runs must be reported before proceeding to report the results of the second wavelength used.

E. CRDL Standard for AA and ICP [FORM II(PART 2)-IN]

This form is used to report analyte recoveries from analyses of the CRDL Standards for AA (CRA) and CRDL Standards for ICP (CRI).

Complete the header information according to the instructions in Part A and as follows.

Enter the AA CRDL Standard Source (12 spaces maximum) and the ICP CRDL Standard Source (12 spaces maximum), as explained in Part D.

Under "CRDL Standard for AA True," enter the value (in ug/L, to one decimal place) of the concentration of each analyte in the CRDL Standard Source Solution that was analyzed.

Under "CRDL Standard for AA Found", enter the value (in ug/L, to two decimal places) of the concentration of each analyte measured in the CRDL Standard Solution.

Under "CRDL Standard for AA %R", enter the value (to one decimal place) of the percent recovery computed according to the following equation:

$$\%R = \frac{\text{Found CRDL Standard for AA}}{\text{True CRDL Standard for AA}} \times 100 \quad (2.3)$$

Under "CRDL Standard for ICP Initial True", enter the value (to one decimal place) of the concentration of each analyte in the CRDL Standard Solution that was analyzed by ICP for analytical samples associated with the SDG. Concentration units are ug/L.

Under "CRDL Standard for ICP Initial Found", enter the value (to two decimal places) of the concentration of each analyte measured in the CRDL Standard Solution analyzed at the beginning of each run. Concentration units are ug/L.

Under "CRDL Standard for ICP, Initial %R" enter the value (to one decimal place) of the percent recovery computed according to the following equation:

$$\%R = \frac{\text{CRDL Standard for ICP Initial Found}}{\text{CRDL Standard for ICP True}} \times 100 \quad (2.4)$$

Under "CRDL Standard for ICP Final Found", enter the value (in ug/L, to two decimal places) of the concentration of each analyte measured in the CRDL Standard Solution analyzed at the end of each run.

Under "CRDL Standard for ICP Final %R", enter the value (to one decimal place) of the percent recovery computed according to the following equation:

$$\%R = \frac{\text{CRDL Standard for ICP Final Found}}{\text{CRDL Standard for ICP True}} \times 100 \quad (2.5)$$

All %R values reported in equations 2.3, 2.4, and 2.5 must be calculated using the exact true and found values reported on this form.

Note that for every initial solution reported there must be a final one. However, the opposite is not true. If a CRDL Standard for ICP (CRI) was required to be analyzed in the middle of a run (to avoid exceeding the 8-hour limit), it must be reported in the "Final Found" section of this form.

If more CRI or CRA analyses were required or analyses were performed using more than one wavelength per analyte, submit additional FORMs II(PART 2)-IN as appropriate.

The order of reporting CRAs and CRIs for each analyte must follow the temporal order in which the standards were run starting with the first Form IIB and continuing to the following Form IIB's as appropriate. The order of reporting CRA and CRI is independent. When multiple wavelengths are used for one analyte, all the results of one wavelength must be reported before proceeding to the next wavelength.

F. Blanks [FORM III-IN]

This form is used to report analyte concentrations found in the Initial Calibration Blank (ICB), in Continuing Calibration Blanks (CCB), and in the Preparation Blank (PB).

Complete the header information according to the instructions in Part A and as follows.

Enter "SOIL" or "WATER" as appropriate as the matrix of the Preparation Blank. No abbreviations or other matrix descriptors may be used.

According to the matrix specified for the Preparation Blank, enter "UG/L" (for water) or "MG/KG" (for soil) as the Preparation Blank concentration units.

Under "Initial Calib. Blank", enter the concentration (in ug/L, to one decimal place) of each analyte in the most recent Initial Calibration Blank.

Under the "C" qualifier field, for any analyte enter "B" if the absolute value of the analyte concentration is less than the CRDL but greater than or equal to the IDL. Enter "U" if the absolute value of the analyte in the blank is less than the IDL.

Under "Continuing Calibration Blank 1", enter the concentration (in ug/L, to one decimal place) of each analyte detected in the first required Continuing Calibration Blank (CCB) analyzed after the Initial Calibration Blank. Enter any appropriate qualifier, as explained for the "Initial Calibration Blank," to the "C" qualifier column immediately following the "Continuing Calibration Blank 1" column.

If only one Continuing Calibration Blank was analyzed, then leave the columns labeled "2" and "3" blank. If up to three CCB's were analyzed, complete the columns labeled "2" and "3", in accordance with the instructions for the "Continuing Calibration Blank 1" column. If more than three Continuing Calibration Blanks were analyzed, then complete additional FORMS III-IN as appropriate.

Under "Preparation Blank", enter the concentration in ug/L (to one decimal place) for a water blank or in mg/Kg (to three decimal places) for a soil blank, of each analyte in the Preparation Blank. Enter any appropriate qualifier, as explained for the "Initial Calibration Blank," to the "C" qualifier column immediately following the "Preparation Blank" column.

For all blanks, enter the concentration of each analyte (positive or negative) measured above the IDL or below the negative value of the IDL.

Under "M", enter the method used, as explained in Part C.

If more than one wavelength is used to analyze an analyte, submit additional FORMS III-IN as appropriate.

The order of reporting ICBs and CCBs for each analyte must follow the temporal order in which the blanks were run starting with the first Form III and moving from left to right and continuing to the following Form III's as explained in Part D. When multiple wavelengths are used for the analysis of one analyte, all the results of one wavelength must be reported before proceeding to the next wavelength.

G. ICP Interference Check Sample [FORM IV-IN]

This form is used to report Interference Check Sample (ICS) results for each ICP instrument used in Sample Delivery Group analyses.

Complete the header information according to the instructions in Part A and as follows:

For "ICP ID Number", enter an identifier that uniquely identifies a specific instrument within the Contractor laboratory. No two ICP instruments within a laboratory may have the same ICP ID Number.

Enter "ICS Source" (12 spaces maximum) as explained in Part D. For EPA solutions include in the source name a number identifying it (e.g., EPA-LV87).

Under "True Sol. A", enter the true concentration (in ug/L, to the nearest whole number) of each analyte present in Solution A.

Under "True Sol. AB", enter the true concentration (in ug/L, to the nearest whole number) of each analyte present in Solution AB.

Under "Initial Found Sol. A", enter the concentration (in ug/L, to the nearest whole number) of each analyte found in the initial analysis of Solution A as required in Exhibit E.

Under "Initial Found Sol. AB", enter the concentration (in ug/L, to one decimal place) of each analyte in the initial analysis of Solution AB as required in Exhibit E.

Under "Initial Found %R", enter the value (to one decimal place) of the percent recovery computed according to the following equation:

$$\%R = \frac{\text{Initial Found Solution AB}}{\text{True Solution AB}} \times 100 \quad (2.6)$$

Under "Final Found Sol. A", enter the concentration (in ug/L, to the nearest whole number) of each analyte found in the final analysis of Solution A as required in Exhibit E.

Under "Final Found Sol. AB", enter the concentration (in ug/L, to one decimal place) of each analyte found in the final analysis of Solution AB as required in Exhibit E.

For All Found values of solutions A and AB, enter the concentration (positive, negative, or zero) of each analyte at each wavelength used for analysis by ICP.

Under "Final Found %R", enter the value (to one decimal place) of the percent recovery computed according to the following equation:

$$\%R = \frac{\text{Final Found Solution AB}}{\text{True Solution AB}} \times 100 \quad (2.7)$$

All %R values reported must be calculated using the exact true and found values reported on this form.

Note that for every initial solution reported there must be a final one. However, the opposite is not true. If an ICS was required to be analyzed in the middle of a run (to avoid exceeding the 8-hour limit), it must be reported in the "Final Found" section of this form.

If more ICS analyses were required, submit additional FORMs IV-IN as appropriate.

The order of reporting ICSs for each analyte must follow the temporal order in which the standards were run starting with the first Form IV and continuing to the following Form IV's as appropriate. The order of reporting ICS is independent. When multiple wavelengths are used for one analyte, all the results of one wavelength must be reported before proceeding to the next wavelength.

H. Spike Sample Recovery [FORM V(PART 1)-IN]

This form is used to report results for the pre-digest spike.

Complete the header information according to the instructions in Part A and as follows.

Indicate the appropriate matrix, level and concentration units (ug/L for water and mg/Kg dry weight for soil) as explained in Parts A and C.

For "%Solids for Sample," enter the percent solids (as explained in Part C) for the original sample of the EPA Sample Number reported on the form. Note that this number must equal the one reported on Form I for that sample.

In the "EPA Sample No." box, enter the EPA Sample Number (7 places maximum) of the sample from which the spike results on this form were obtained. The number must be centered in the box.

Under "Control Limit %R", enter "75-125" if the spike added value was greater than or equal to one-fourth of the sample result value. If not, leave the field empty.

Under "Spiked Sample Result (SSR)", enter the measured value (to four decimal places), in appropriate units, for each analyte in the matrix spike-sample. Enter any appropriate qualifier, as explained in Part C, to the "C" qualifier column immediately following the "Spiked Sample Result (SSR)" column.

Under "Sample Result (SR)", enter the measured value (to four decimal places) for each required analyte in the sample (reported in the EPA Sample No. box) on which the matrix spike was performed. Enter any appropriate qualifier, as explained in Part C, to the "C" qualifier column immediately following the "Sample Result (SR)" column.

Under "Spike Added (SA)", enter the value (to two decimal places) for the concentration of each analyte added to the sample. The same concentration units must be used for spiked sample results, unspiked (original sample) results, and spike added sample results. If the "spike added" concentration is specified in the contract, the value added and reported must be that specific concentration in appropriate units.

Under "%R", enter the value (to one decimal place) of the percent recovery for all spiked analytes computed according to the following equation:

$$\%R = \frac{(SSR - SR)}{SA} \times 100 \quad (2.8)$$

%R must be reported, whether it is negative, positive or zero.

The values for SSR, SR, and SA must be exactly those reported on this form. A value of zero must be used for SSR or SR if the analyte value is less than the IDL.

Under "Q", enter "N" if the Spike Recovery (%R) is out of the control limits (75-125) and the Spike Added (SA) is greater than or equal to one-fourth of the Sample Result (SR).

Under "M", enter the method used (as explained in Part C) or enter "NR" if the analyte is not required in the spike.

If different samples were used for spike sample analysis of different analytes, additional FORMS V(PART 1)-IN must be submitted for each sample as appropriate.

I. Post Digest Spike Sample Recovery [FORM V(PART 2)-IN]

This form is used to report results for the post-digest spike recovery which is based upon the addition of a known quantity of analyte to an aliquot of the digested sample.

Complete the header information according to the instructions in Part A and as follows.

In the "EPA Sample No." box, enter the EPA Sample Number (7 spaces maximum) of the sample from which the spike results on this form were obtained. The number must be centered in the box.

The "Control Limit %R" and "Q" fields must be left blank until limits are established by EPA. At that time, the Contractor will be informed how to complete these fields.

Under "Spiked Sample Result (SSR)", enter the measured value (in ug/L, to two decimal places) for each analyte in the post-digest spike sample. Enter any appropriate qualifier, as explained in Part C, to the "C" qualifier column immediately following the "Spiked Sample Result (SSR)" column.

Under "Sample Result (SR)", enter the measured value (in ug/L, to two decimal places) for the concentration of each analyte in the sample (reported in the EPA Sample No. box) on which the spike was performed. Enter any appropriate qualifier, as explained in Part C, to the "C" qualifier column immediately following the "Sample Result (SR)" column.

Under "Spike Added (SA)", enter the value (in ug/L, to one decimal place) for each analyte added to the sample. The same concentration units must be used for spiked sample results, unspiked (original sample) results, and spike added sample results. If the spike added concentration is specified in the contract, the value added and reported must be that specific concentration in appropriate units.

Under "%R", enter the value (to one decimal place) of the percent recovery for all spiked analytes computed according to Equation 2.8 in Part H, preceding.

%R must be reported, whether it is negative, positive or zero.

The values for SSR, SR, and SA must be exactly those reported on this form. A value of zero must be substituted for SSR or SR if the analyte value is less than the IDL.

Under "M", enter the method used as explained in Part C, or enter "NR" if the spike was not required.

If different samples were used for spike sample analysis of different analytes, additional FORMS V(PART 1)-IN must be submitted.

J. Duplicates [FORM VI-IN]

The duplicates form is used to report results of duplicate analyses. Duplicate analyses are required for % solids values and all analyte results.

Complete the header information according to the instructions in Part A and as follows.

Indicate the appropriate matrix, level and concentration units (ug/L for water and mg/Kg dry weight for soil) as explained in Parts A and C.

For "% Solids for Sample," enter to percent solids (as explained in Part C) for the original sample of the EPA Sample Number reported on the form. Note that this number must equal the one reported on Form I for that sample.

For "% Solids for Duplicate," enter the percent solids (as explained in Part C) for the duplicate sample of the EPA Sample Number reported on the form.

In the "EPA Sample No." box, enter the EPA Sample Number (7 spaces maximum) of the sample from which the duplicate sample results on this form were obtained. The number must be centered in the box.

Under "Control Limit", enter the CRDL (in appropriate units, ug/L for water or mg/kg dry weight basis compared to the original sample weight and percent solids) for the analyte if the sample or duplicate values were less than 5x CRDL. If the sample and duplicate values were less than the CRDL or greater than or equal to 5x CRDL, leave the field empty.

Under Sample (S), enter the original measured value (to four decimal places) for the concentration of each analyte in the sample (reported in the EPA Sample No. box) on which a Duplicate analysis was performed. Concentration units are those specified on the form. Enter any appropriate qualifier, as explained in Part C, to the "C" qualifier column immediately following the "Sample (S)" column.

Under Duplicate (D), enter the measured value (to four decimal places) for each analyte in the Duplicate sample. Concentration units are those specified on the form. Enter any appropriate qualifier, as explained in Part C, to the "C" qualifier column immediately following the "Duplicate (D)" column.

For solid samples, the concentration of the original sample must be computed using the weight and % solids of the original sample. The concentration of the duplicate sample must be computed using the weight and % solids of the duplicate sample.

Under RPD, enter the absolute value (to one decimal place) of the Relative Percent Difference for all analytes detected above the IDL in either the sample or the duplicate, computed according to the following equation:

$$RPD = \frac{|S - D|}{(S + D)/2} \times 100 \quad (2.9)$$

The values for S and D must be exactly those reported on this form. A value of zero must be substituted for S or D if the analyte concentration is less than the IDL in either one. If the analyte concentration is less than the IDL in both S and D, leave the RPD field empty.

Under "Q", enter "*" if the duplicate analysis for the analyte is out of control. If both sample and duplicate values are greater than or equal to 5x CRDL, then the RPD must be less than or equal to 20% to be in control. If either sample or duplicate values are less than 5x CRDL, then the absolute difference between the two values must be less than the CRDL to be in control. If both values are below the CRDL, then no control limit is applicable.

Under "M", enter method used as explained in Part C.

K. Laboratory Control Sample [FORM VII-IN]

This form is used to report results for the solid and aqueous Laboratory Control Samples.

Complete the header information according to the instructions in Part A and as follows.

For the Solid LCS Source (12 spaces maximum), enter "EPA0387" if the EPA provided standard was used. Substitute an appropriate number provided by the EPA for LCS solutions prepared in the future. If other sources were used, complete as explained in Part D. For the Aqueous LCS Source, enter the source name (12 spaces maximum) as explained in Part D.

Under "Aqueous True", enter the value (in ug/L, to one decimal place) of the concentration of each analyte in the Aqueous LCS Standard Source.

Under "Aqueous Found", enter the measured concentration (in ug/L, to two decimal places) of each analyte found in the Aqueous LCS solution.

Under "Aqueous %R", enter the value of the percent recovery (to one decimal place) computed according to the following equation:

$$\%R = \frac{\text{Aqueous LCS Found}}{\text{Aqueous LCS True}} \times 100 \quad (2.10)$$

Under "Solid True", enter the value (in mg/Kg, to one decimal place) of the concentration of each analyte in the Solid LCS Source.

Under "Solid Found", enter the measured value (in mg/Kg, to one decimal place) of each analyte found in the Solid LCS solution.

Under "C", enter "B" or "U" or leave empty, to describe the found value of the solid LCS as explained in Part C.

Under "Limits", enter the lower limit (in mg/Kg, to one decimal place) in the left column, and the upper limit (in mg/Kg, to one decimal place) in the right column, for each analyte in the Solid LCS Source solution.

Under "Solid %R", enter the value of the percent recovery (to one decimal place) computed according to the following equation:

$$\%R = \frac{\text{Solid LCS Found}}{\text{Solid LCS True}} \times 100 \quad (2.11)$$

The values for true and found aqueous and solid LCS's used in equations 2.10 and 2.11 must be exactly those reported on this form. If the analyte concentration is less than the IDL, a value of zero must be substituted for the solid LCS found.

Submit additional FORMs VII-IN as appropriate, if more than one aqueous LCS or solid LCS was required.

L. Standard Addition Results [FORM VIII-IN]

This form is used to report the results of samples analyzed using the Method of Standard Additions (MSA) for Furnace AA analysis.

Complete the header information according to the instructions in Part A.

Under "EPA Sample No.", enter the EPA Sample Numbers (7 spaces maximum) of all analytical samples analyzed using the MSA. This includes reruns by MSA (if the first MSA was out of control) as explained in Exhibit E.

Note that only field samples and duplicates may be reported on this form, thus the EPA Sample Number usually has no suffix or a "D."

A maximum of 32 samples can be entered on this form. If additional samples required MSA, submit additional FORMs VIII-IN. Samples must be listed in alphanumeric order per analyte, continuing to the next FORM VIII-IN if applicable.

Under "An", enter the chemical symbol (2 spaces maximum) for each analyte for which MSA was required for each sample listed. The analytes must be in alphabetic listing of the chemical symbols.

Results for different samples for each analyte must be reported sequentially, with the analytes ordered according to the alphabetic listing of their chemical symbols. For instance, results for As (arsenic) in samples MAA110, MAA111, and MAA112 would be reported in sequence, followed by the result for Pb (lead) in MAA110 etc.

Under "0 ADD ABS", enter the measured value in absorbance units (to three decimal places) for the analyte before any addition is performed.

Under "1 ADD CON", enter the final concentration in ug/L (to two decimal places) of the analyte (excluding sample contribution) after the first addition to the sample analyzed by MSA.

Under "1 ADD ABS", enter the measured value (in the same units and decimal places as "0 ADD ABS") of the sample solution spiked with the first addition.

Under "2 ADD CON", enter the final concentration in ug/L (to two decimal places) of the analyte (excluding sample contribution) after the second addition to the sample analyzed by MSA.

Under "2 ADD ABS", enter the measured value (in the same units and decimal places as "0 ADD ABS") of the sample solution spiked with the second addition.

Under "3 ADD CON", enter the final concentration in ug/L (to two decimal places) of the analyte (excluding sample contribution) after the third addition to the sample analyzed by MSA.

Under "3 ADD ABS", enter the measured value (in the same units and decimal places as "0 ADD ABS") of the sample solution spiked with the third addition.

Note that "0 ADD ABS", "1 ADD ABS", "2 ADD ABS", and "3 ADD ABS" must have the same dilution factor.

Under "Final Conc.", enter the final analyte concentration (in ug/L, to one decimal place) in the sample as determined by MSA computed according to the following formula:

$$\text{Final Conc.} = (\text{x-intercept}) \times \text{DIL} \quad (2.12)$$

Note that the final concentration of an analyte does not have to equal the value for that analyte which is reported on FORM I-IN for that sample.

Under "r", enter the correlation coefficient (to four decimal places) that is obtained for the least squares regression line representing the following points (x,y):(0.0, "0 ADD ABS"), ("1 ADD CON", "1 ADD ABS"), ("2 ADD CON", "2 ADD ABS"), ("3 ADD CON", "3 ADD ABS").

Note that the correlation coefficient must be calculated using the ordinary least squares linear regression (unweighted) according to the following formula:

$$r = \frac{N \sum x_i y_i - \sum x_i \sum y_i}{\sqrt{[N \sum x_i^2 - (\sum x_i)^2] [N \sum y_i^2 - (\sum y_i)^2]}} \quad (2.13)$$

Under "Q", enter "+" if r is less than 0.995. If r is greater than or equal to 0.995, then leave the field empty.

M. ICP Serial Dilution [FORM IX-IN]

This form is used to report results for ICP serial dilution.

Complete the header information according to the instructions in Part A and as follows.

In the "EPA Sample No." box, enter the EPA Sample Number (7 places maximum) of the sample for which serial dilution analysis results on this form were obtained. The number must be centered in the box.

Under "Initial Sample Result (I)", enter the measured value (in ug/L, to two decimal places) for each ICP analyte in the undiluted sample (for the EPA sample number reported on this form). Enter any appropriate qualifier, as explained in Part C, to the "C" qualifier column immediately following the "Initial Sample Result (I)" column.

Note that the Initial Sample Concentration for an analyte does not have to equal the value for that analyte reported on FORM I-IN for that sample. It is the value of the analyte concentration (uncorrected for dilution) that is within the linear range of the instrument.

Under "Serial Dilution Result (S)", enter the measured concentration value (in ug/L, to two decimal places) for each ICP analyte in the diluted sample. The value must be adjusted for that dilution. Enter any appropriate qualifier, as explained in Part B, to the "C" qualifier column immediately following the "Serial Dilution Result (S)" column.

Note that the Serial Dilution Result (S) is obtained by multiplying by five the instrument measured value (in ug/L) of the serially diluted sample and that the "C" qualifier for the serial dilution must be established based on the serial dilution result before correcting it for the dilution regardless of the value reported on the form.

Under "% Difference", enter the absolute value (to one decimal place) of the percent difference in concentration of required analytes, between the original sample and the diluted sample (adjusted for dilution) according to the following formula:

$$\% \text{ Difference} = \frac{|I - S|}{I} \times 100 \quad (2.14)$$

The values for I and S used to calculate % Difference in equation 2.14 must be exactly those reported on this form. A value of zero must be substituted for S if the analyte concentration is less than the IDL. If the analyte concentration in (I) is less than the IDL, concentration leave "% Difference" field empty.

Under "Q", enter "E" if the % Difference is greater than 10% and the original sample concentration (reported on FORM I-IN) is greater than 50x the IDL reported on FORM XI-IN.

Under "M", enter the method of analysis for each analyte as explained in Part C.

N. Instrument Detection Limits (Quarterly) [FORM X-IN]

This form documents the Instrument Detection Limits for each instrument that the laboratory used to obtain data for the Sample Delivery Group. Only the instrument and wavelengths used to generate data for the SDG must be included.

Although the Instrument Detection Limits (IDLs) are determined quarterly (every three calendar months) a copy of the quarterly instrument detection limits must be included with each SDG data package on FORM(s) X-IN.

Complete the header information according to the instructions in Part A and as follows.

Enter the date (formatted MM/DD/YY) on which the IDL values were obtained (or became effective).

Enter ICP ID Number, Flame AA ID Number, and Furnace AA ID Number (12 spaces maximum each). These ID Numbers are used to uniquely identify each instrument that the laboratory uses to do CLP work.

Under "Wavelength", enter the wavelength in nanometers (to two decimal places) for each analyte for which an Instrument Detection Limit (IDL) has been established and is listed in the IDL column. If more than one wavelength is used for an analyte, use other FORMs XI-IN as appropriate to report the Instrument Detection Limit.

Under "Background", enter the type of background correction used to obtain Furnace AA data. Enter "BS" for Smith Hieftje, "BD" for Deuterium Arc, or "BZ" for Zeeman background correction.

Contract Required Detection Limits (in ug/L) as established in Exhibit C, must appear in the column headed "CRDL".

Under "IDL", enter the Instrument Detection Limit (ug/L, to one decimal place) as determined by the laboratory for each analyte analyzed by the instrument for which the ID Number is listed on this form. Except for Mercury, the instrument detection limit must be rounded to a whole number.

Under "M", enter the method of analysis used to determine the instrument detection limit for each wavelength used. Use appropriate codes as explained in Part C.

Use additional FORMs X-IN if more instruments and wavelengths are used. Note that the date on this form must not exceed the analysis dates in the SDG data package or precede them by more than three months.

Use the Comments section to indicate alternative wavelengths and the conditions under which they are used.

0. ICP Interelement Correction Factors (Annually) [FORM XI(PART 1)-IN]

This form documents for each ICP instrument the interelement correction factors applied by the Contractor laboratory to obtain data for the Sample Delivery Group.

Although the correction factors are determined annually (every twelve calendar months), a copy of the results of the annual interelement correction factors must be included with each SDG data package on FORM XI(PART 1)-IN.

Complete the header information according to instructions in Part A and as follows.

Enter the ICP ID Number (12 spaces maximum), which is a unique number designated by the laboratory to identify each ICP instrument used to produce data in the SDG package. If more than one ICP instrument is used, submit additional FORMs XI(PART 1)-IN as appropriate.

Report the date (formatted as MM/DD/YY) on which these correction factors were determined for use. This date must not exceed the ICP analysis dates in the SDG data package or precede them by more than twelve calendar months.

Under "Wavelength", list the wavelength in nanometers (to two decimal places) used for each ICP analyte. If more than one wavelength is used, submit additional FORMs XI(PART 1)-IN as appropriate.

Under "Al", "Ca", "Fe", "Mg", enter the correction factor (negative, positive or zero, to seven decimal places, 10 spaces maximum) for each ICP analyte. If correction factors for another analyte are applied, use the empty column and list the analyte's chemical symbol in the blank two-space header field provided for that column.

If corrections are not applied for an analyte, a zero must be entered for that analyte to indicate that the corrections were determined to be zero. If correction factors are applied for more than one additional analyte, use FORM XI(PART 2)-IN.

P. ICP Interelement Correction Factors (Annually) [FORM XI(PART 2)-IN]

This form is used if correction factors for analytes other than Al, Ca, Fe, Mg, and one more analyte of the Contractor's choice, were applied to the analytes analyzed by ICP. Complete this form as for FORM XI(PART 1)-IN by listing the chemical symbol for additional analytes in the heading of the empty columns in the two-space fields provided.

Columns of correction factors for additional analytes must be entered left to right starting on FORM XI(PART 1)-IN and proceeding to FORM XI(PART 2)-IN, according to the alphabetic order of their chemical symbols. Note that correction factors for Al, Ca, Fe, and Mg are all required and are to be listed first (as they appear on FORM XI(PART 1)-IN).

Q. ICP Linear Ranges (Quarterly) [FORM XII-IN]

This form documents the quarterly linear range analysis for each ICP instrument that the laboratory used to obtain data for the SDG.

Complete the header information according to the instructions in Part A and as follows.

Enter the ICP ID Number (12 spaces maximum), which is a unique number designated by the Contractor to identify each ICP instrument used to produce data for the SDG. If more than one ICP instrument is used, submit additional FORMs XII-IN as appropriate.

Report the date (formatted as MM/DD/YY) on which these linear ranges were determined for use. This date must not exceed the dates of analysis by ICP in the SDG data package and must not precede the analysis dates by more than three calendar months.

Under "Integ. Time (Sec.)," enter the integration time (in seconds to two decimal places) used for each measurement taken from the ICP instrument.

Under "Concentration", enter the concentration (in ug/L) that is the upper limit of the ICP instrument linear range as determined in Exhibit E. Any measurement in the SDG data package at or below this concentration is within the linear range. Any measurement above it is out of the linear range, and thus, is an estimated value and must be diluted into the linear range.

Under "M", enter "NR" for analytes analyzed by methods other than ICP. No entries are required under "M" for analytes analyzed by ICP.

If more instruments or analyte wavelengths are used, submit additional FORMs XII-IN as appropriate.

R. Preparation Log [Form XIII-IN]

This Form is used to report the preparation run log.

All field samples and all quality control preparations (including duplicates, spikes, LCS's, PB's and repreparations) associated with the SDG must be reported on Form XIII.

Submit one Form XIII per method if no more than thirty-two preparations, including quality control preparations, were performed. If more than thirty-two preparations per method were performed, then submit additional Forms XIII as appropriate.

Complete the header information according to the instructions in Part A, and as follows:

For "Method", enter the method of analysis (two characters maximum) for which the preparations listed on the Form were made. Use appropriate method codes as specified in Part C.

Under "EPA Sample No.", enter the EPA Sample Number of each sample in the SDG, and of all other preparations such as duplicates, spikes, LCSs, PBs, and repreparations (all formatted according to Table 1). All EPA Sample Numbers must be listed in ascending alphanumeric order, continuing to the next Form XIII if applicable. If a sample was reprepared, list the same EPA Sample Number in the order of increasing preparation date.

Under "Preparation Date", enter the date (formatted MM/DD/YY) on which each sample was prepared for analysis by the method indicated in the header section of the Form.

Under "Weight", enter the wet weight (in grams, to two decimal places) of each soil sample prepared for analysis by the method indicated in the header section of the Form. If the sample matrix is water, then leave the field empty.

Under "Volume", enter the final volume (in mL, to the nearest whole number) of the preparation for each sample prepared for analysis by the method indicated in the header section of the Form. This field must have a value for each sample listed.

S. Analysis Run Log [Form XIV-IN]

This Form is used to report the sample analysis run log.

A run is defined as the totality of analyses performed by an instrument throughout the sequence initiated by, and including, the first SOW-required calibration standard and terminated by, and including, the continuing calibration verification and blank following the last SOW-required analytical sample.

All field samples and all quality control analyses (including calibration standards, ICVs, CCVs, ICBs, CCBs, CRAs, CRIs, ICSs, LRSs, LCSs, PBs, duplicates, serial dilutions, pre-digestion spikes, post-digestion spikes, analytical spikes, and each addition analyzed for the method of standard addition determination) associated with the SDG must be reported on Form XIV. The run must be continuous and inclusive of all analyses performed on the particular instrument during the run.

Submit one Form XIV per run if no more than thirty-two (32) analyses, including instrument calibration, were analyzed in the run. If more than thirty-two analyses were performed in the run, submit additional Forms XIV as appropriate.

Complete the header information according to the instructions in Part A, and as follows:

For "Instrument ID Number", enter the instrument ID number, (12 spaces maximum), which must be an identifier designated by the laboratory to uniquely identify each instrument used to produce data which are required to be reported in the SDG deliverable. If more than one instrument is used, submit additional Forms XIV as appropriate.

For "Method", enter the method code (two characters maximum) according to the specifications in Part C.

For "Start Date", enter the date (formatted MM/DD/YY) on which the analysis run was started.

For "End Date", Enter the date (formatted MM/DD/YY) on which the analysis run was ended.

Under "EPA Sample No.", enter the EPA sample number of each analysis, including all QC operations applicable to the SDG (formatted according to Table 1). All EPA Sample Numbers must be listed in increasing temporal (date and time) order of analysis, continuing to the next Form XIV for the instrument run if applicable. The analysis date and time of other analyses not associated with the SDG, but analyzed by the instrument in the reported analytical run, must be reported. Those analyses must be identified with the EPA Sample No. of "ZZZZZ".

Under "D/F", enter the dilution factor (to two decimal places) by which the final digestate or distillate needed to be diluted for each analysis be performed. The dilution factor does not include the dilution inherent in the preparation as specified by the preparation procedures in Exhibit D.

Note that for a particular sample a dilution factor of "1" must be entered if the digestate or distillate were analyzed without adding any further volume of dilutant or any other solutions to the "Volume" or an aliquot of the "Volume" listed on Form XIII for that sample.

For EPA supplied solutions such as ICVs, ICSs, and LCSs, a dilution factor must be entered if the supplied solution had to be diluted to a dilution different from that specified by the instructions provided with the solution. The dilution factor reported in such a case must be that which would make the reported true values on the appropriate form for the solution equal those that were supplied with the solution by the EPA. For instance, ICV-2(0887) has a true value of 104.0 ug/L at a 20 fold dilution. If the solution is prepared at a 40 fold dilution, a dilution factor of "2" must be entered on Form XIV and the uncorrected instrument reading is compared to a true value of 52 ug/L. In this example, Form II will have a true value of 104.0 regardless of the dilution used. The found value for the ICV must be corrected for the dilution listed on Form XIV using the following formula:

Found value on Form II - Instrument readout in ug/L x D/F

Under "Time", enter the time, (in military format - HHMM), at which each analysis was performed. If an auto sampler is used with equal analysis time and intervals between analyses, then only the start time of the run (the time of analysis of the first calibration standard) and end time of the run (the time of analysis of the final CCV or CCB, which ever is later) need to be reported.

Under "% R", enter the percent recovery (to one decimal place) for each Furnace AA analytical spike analyzed. If the analytical spike was performed on more than one analyte, use additional Forms XIV as appropriate. Leave the "% R" field empty if the analysis reported is not for an analytical spike.

Under "Analytes", enter "X" in the column of the designated analyte to indicate that the analyte value was used from the reported analysis to report data in the SDG. Leave the column empty for each analyte if the analysis was not used to report the particular analyte.

SECTION IV
DATA REPORTING FORMS

U. S. EPA - CLP

Job Name: _____

Contract:

Lab Code: _____

Case No.:

SAS No.:

SDG No.:

SOW No.

Lab Sample ID

[illegible][illegible]

Were ICP background corrections applied? Yes/No

If yes, were raw data generated before application of background corrections?

Comments: _____

I certify that this data package is in compliance with the terms and conditions of the contract, both technically and for completeness, for other than the conditions detailed above. Release of the data contained in this hardcopy data package and in the computer-readable data submitted on floppy diskette has been authorized by the Laboratory Manager or the Manager's designee, as verified by the following signature.

Signature: _____

Name: _____

Date:

Title:

COVER PAGE - IN

U.S. EPA - CLP

1
INORGANIC ANALYSIS DATA SHEET

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix (soil/water): _____ Lab Sample ID: _____

Level (low/med): _____ Date Received: _____

% Solids: _____

Concentration Units (ug/L or mg/kg dry weight): _____

CAS No.	Analyte	Concentration	C	Q	M
7429-90-5	Aluminum				
7440-36-0	Antimony				
7440-38-2	Arsenic				
7440-39-3	Barium				
7440-41-7	Beryllium				
7440-43-9	Cadmium				
7440-70-2	Calcium				
7440-47-3	Chromium				
7440-48-4	Cobalt				
7440-50-8	Copper				
7439-89-6	Iron				
7439-92-1	Lead				
7439-95-4	Magnesium				
7439-96-5	Manganese				
7439-97-6	Mercury				
7440-02-0	Nickel				
7440-09-7	Potassium				
7782-49-2	Selenium				
7440-22-4	Silver				
7440-23-5	Sodium				
7440-28-0	Thallium				
7440-62-2	Vanadium				
7440-66-6	Zinc				
	Cyanide				

Color Before: _____ Clarity Before: _____ Texture: _____

Color After: _____ Clarity After: _____ Artifacts: _____

Comments:

U.S. EPA - CLP

2A

INITIAL AND CONTINUING CALIBRATION VERIFICATION

Lab Name: _____ Contract: _____
 Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____
 Initial Calibration Source: _____
 Continuing Calibration Source: _____

Concentration Units: ug/L

Analyte	Initial Calibration			Continuing Calibration					M
	True	Found	%R(1)	True	Found	%R(1)	Found	%R(1)	
Aluminum									
Antimony									
Arsenic									
Barium									
Beryllium									
Cadmium									
Calcium									
Chromium									
Cobalt									
Copper									
Iron									
Lead									
Magnesium									
Manganese									
Mercury									
Nickel									
Potassium									
Selenium									
Silver									
Sodium									
Thallium									
Vanadium									
Zinc									
Cyanide									

(1) Control Limits: Mercury 80-120; Other Metals 90-110; Cyanide 85-115

U.S. EPA - CLP

2B

CRDL STANDARD FOR AA AND ICP

Lab Name: _____

Contract: _____

Lab Code: _____

Case No.: _____

SAS No.: _____

SDG No.: _____

AA CRDL Standard Source: _____

ICP CRDL Standard Source: _____

Concentration Units: ug/L

Analyte	CRDL Standard for AA			CRDL Standard for ICP				
	True	Found	%R	True	Initial Found	%R	Final Found	%R
Aluminum								
Antimony								
Arsenic								
Barium								
Beryllium								
Cadmium								
Calcium								
Chromium								
Cobalt								
Copper								
Iron								
Lead								
Magnesium								
Manganese								
Mercury								
Nickel								
Potassium								
Selenium								
Silver								
Sodium								
Thallium								
Vanadium								
Zinc								

U.S. EPA - CLP

3
BLANKS

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Preparation Blank Matrix (soil/water): _____

Preparation Blank Concentration Units (ug/L or mg/kg): _____

Analyte	Initial Calib. Blank (ug/L)	C	Continuing Calibration Blank (ug/L)						Prepa- ration Blank	C	M
			1	C	2	C	3	C			
Aluminum											
Antimony											
Arsenic											
Barium											
Beryllium											
Cadmium											
Calcium											
Chromium											
Cobalt											
Copper											
Iron											
Lead											
Magnesium											
Manganese											
Mercury											
Nickel											
Potassium											
Selenium											
Silver											
Sodium											
Thallium											
Vanadium											
Zinc											
Cyanide											

FORM III - IN

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U.S. EPA - CLP

4

ICP INTERFERENCE CHECK SAMPLE

Lab Name: _____

Contract: _____

Lab Code: _____

Case No: _____

SAS No.: _____

SDG No.: _____

ICP ID Number: _____

ICS Source: _____

Concentration Units: ug/L

Analyte	True		Initial Found			Final Found		
	Sol. A	Sol. AB	Sol. A	Sol. AB	%R	Sol. A	Sol. AB	%R
Aluminum								
Antimony								
Arsenic								
Barium								
Beryllium								
Cadmium								
Calcium								
Chromium								
Cobalt								
Copper								
Iron								
Lead								
Magnesium								
Manganese								
Mercury								
Nickel								
Potassium								
Selenium								
Silver								
Sodium								
Thallium								
Vanadium								
Zinc								

U. S. EPA - CLP

5A
SPIKE SAMPLE RECOVERY

EPA SAMPLE NO.

Lab Name: _____

Contract: _____

Lab Code: _____

Case No.: _____

SAS No.: _____

SDG No.: _____

Matrix: _____

Level (low/med): _____

‡ Solids for Sample: _____

Concentration Units (ug/L or mg/kg dry weight): _____

Analyte	Control Limit ‡R	Spiked Sample Result (SSR)	C	Sample Result (SR)	C	Spike Added (SA)	‡R	Q	M
Aluminum									
Antimony									
Arsenic									
Barium									
Beryllium									
Cadmium									
Calcium									
Chromium									
Cobalt									
Copper									
Iron									
Lead									
Magnesium									
Manganese									
Mercury									
Nickel									
Potassium									
Selenium									
Silver									
Sodium									
Thallium									
Vanadium									
Zinc									
Cyanide									

Comments:

U. S. EPA - CLP

5B

POST DIGEST SPIKE SAMPLE RECOVERY

EPA SAMPLE NO.

Lab Name: _____

Contract: _____

--

Lab Code: _____

Case No.: _____

SAS No.: _____

SDG No.: _____

Matrix: _____

Level (low/med): _____

Concentration Units: ug/L

Analyte	Control Limit %R	Spiked Sample Result (SSR)	C	Sample Result (SR)	C	Added (SA)	%R	Q	M
Aluminum									
Antimony									
Arsenic									
Barium									
Beryllium									
Cadmium									
Calcium									
Chromium									
Cobalt									
Copper									
Iron									
Lead									
Magnesium									
Manganese									
Mercury									
Nickel									
Potassium									
Selenium									
Silver									
Sodium									
Thallium									
Vanadium									
Zinc									

Comments:

U.S. EPA - CLP

6
DUPLICATES

EPA SAMPLE NO.

Lab Name: _____ Contract: _____
 Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____
 Matrix (soil/water): _____ Level (low/med): _____
 ‡ Solids for Sample: _____ % Solids for Duplicate: _____

Concentration Units (ug/L or mg/kg dry weight): _____

Analyte	Control Limit	Sample (S)	C	Duplicate (D)	C	RPD	Q	M
Aluminum								
Antimony								
Arsenic								
Barium								
Beryllium								
Cadmium								
Calcium								
Chromium								
Cobalt								
Copper								
Iron								
Lead								
Magnesium								
Manganese								
Mercury								
Nickel								
Potassium								
Selenium								
Silver								
Sodium								
Thallium								
Vanadium								
Zinc								
Cyanide								

U.S. EPA - CLP

7
LABORATORY CONTROL SAMPLE

Lab Name: _____ Contract: _____
 Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____
 Solid LCS Source: _____
 Aqueous LCS Source: _____

Analyte	Aqueous (ug/L)			Solid (mg/kg)					%R
	True	Found	%R	True	Found	C	Limits		
Aluminum									
Antimony									
Arsenic									
Barium									
Beryllium									
Cadmium									
Calcium									
Chromium									
Cobalt									
Copper									
Iron									
Lead									
Magnesium									
Manganese									
Mercury									
Nickel									
Potassium									
Selenium									
Silver									
Sodium									
Thallium									
Vanadium									
Zinc									
Cyanide									

U.S. EPA - CLP

9
ICP SERIAL DILUTIONS

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix (soil/water): _____ Level (low/med): _____

Concentration Units: ug/L

Analyte	Initial Sample Result (I)	C	Serial Dilution Result (S)	C	% Differ- ence	Q	M
Aluminum							
Antimony							
Arsenic							
Barium							
Beryllium							
Cadmium							
Calcium							
Chromium							
Cobalt							
Copper							
Iron							
Lead							
Magnesium							
Manganese							
Mercury							
Nickel							
Potassium							
Selenium							
Silver							
Sodium							
Thallium							
Vanadium							
Zinc							

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10

Instrument Detection Limits (Quarterly)

Lab Name: _____ Contract: _____
Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____
ICP ID Number: _____ Date: _____
Flame AA ID Number: _____
Furnace AA ID Number: _____

Analyte	Wave-length (nm)	Back-ground	CRDL (ug/L)	IDL (ug/L)	M
Aluminum			200		
Antimony			60		
Arsenic			10		
Barium			200		
Beryllium			5		
Cadmium			5		
Calcium			5000		
Chromium			10		
Cobalt			50		
Copper			25		
Iron			100		
Lead			3		
Magnesium			5000		
Manganese			15		
Mercury			0.2		
Nickel			40		
Potassium			5000		
Selenium			5		
Silver			10		
Sodium			5000		
Thallium			10		
Vanadium			50		
Zinc			20		

Comments:

FORM X - IN

U. S. EPA - CLP

11A

ICP Interelement Correction Factors (Annually)

Lab Name: _____ Contract: _____
 Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____
 ICP ID Number: _____ Date: _____

Analyte	Wave-length (nm)	Interelement Correction Factors for:				
		Al	Ca	Fe	Mg	---
Aluminum						
Antimony						
Arsenic						
Barium						
Beryllium						
Cadmium						
Calcium						
Chromium						
Cobalt						
Copper						
Iron						
Lead						
Magnesium						
Manganese						
Mercury						
Nickel						
Potassium						
Selenium						
Silver						
Sodium						
Thallium						
Vanadium						
Zinc						

Comments:

U. S. EPA - CLP

11B

ICP Interelement Correction Factors (Annually)

Lab Name: _____ Contract: _____
 Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____
 ICP ID Number: _____ Date: _____

Analyte	Wave-length (nm)	Interelement Correction Factors for:				
		---	---	---	---	---
Aluminum						
Antimony						
Arsenic						
Barium						
Beryllium						
Cadmium						
Calcium						
Chromium						
Cobalt						
Copper						
Iron						
Lead						
Magnesium						
Manganese						
Mercury						
Nickel						
Potassium						
Selenium						
Silver						
Sodium						
Thallium						
Vanadium						
Zinc						

Comments:

U. S. EPA - CLP

12

ICP Linear Ranges (Quarterly)

Lab Name: _____ Contract: _____
 Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____
 ICP ID Number: _____ Date: _____

Analyte	Integ. Time (sec.)	Concentration (ug/L)	M
Aluminum			
Antimony			
Arsenic			
Barium			
Beryllium			
Cadmium			
Calcium			
Chromium			
Cobalt			
Copper			
Iron			
Lead			
Magnesium			
Manganese			
Mercury			
Nickel			
Potassium			
Selenium			
Silver			
Sodium			
Thallium			
Vanadium			
Zinc			

Comments:

13
PREPARATION LOG

[illegible]

14
ANALYSIS RUN LOG

[illegible]

EXHIBIT C

INORGANIC TARGET ANALYTE LIST

INORGANIC TARGET ANALYTE LIST (TAL)

Analyte	Contract Required Detection Limit (1,2) (ug/L)
Aluminum	200
Antimony	60
Arsenic	10
Barium	200
Beryllium	5
Cadmium	5
Calcium	5000
Chromium	10
Cobalt	50
Copper	25
Iron	100
Lead	3
Magnesium	5000
Manganese	15
Mercury	0.2
Nickel	40
Potassium	5000
Selenium	5
Silver	10
Sodium	5000
Thallium	10
Vanadium	50
Zinc	20
Cyanide	10

- (1) Subject to the restrictions specified in the first page of Part G, Section IV of Exhibit D (Alternate Methods - Catastrophic Failure) any analytical method specified in SOW Exhibit D may be utilized as long as the documented instrument or method detection limits meet the Contract Required Detection Limit (CRDL) requirements. Higher detection limits may only be used in the following circumstance:

If the sample concentration exceeds five times the detection limit of the instrument or method in use, the value may be reported even though the instrument or method detection limit may not equal the Contract Required Detection Limit. This is illustrated in the example below:

For lead:

Method in use - ICP

Instrument Detection Limit (IDL) - 40

Sample concentration - 220

Contract Required Detection Limit (CRDL) - 3

The value of 220 may be reported even though instrument detection limit is greater than CRDL. The instrument or method detection limit must be documented as described in Exhibit E.

- (2) The CRDL are the instrument detection limits obtained in pure water that must be met using the procedure in Exhibit E. The detection limits for samples may be considerably higher depending on the sample matrix.

EXHIBIT D

ANALYTICAL METHODS

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SECTION I

INTRODUCTION

Inorganic Methods Flow Chart: Figure I outlines the general analytical scheme the Contractor will follow in performing analyses under this contract.

Permitted Methods: Subject to the restrictions specified in Section IV, Part G - Alternate Methods (Catastrophic ICP Failure), any analytical method specified in Exhibit D may be used as long as the documented instrument or method detection limits meet the Contract Required Detection Limits (Exhibit C). Analytical methods with higher detection limits may be used only if the sample concentration exceeds five times the documented detection limit of the instrument or method.

Initial Run Undiluted: All samples must initially be run undiluted (i.e., final product of the sample preparation procedure). When an analyte concentration exceeds the calibrated or linear range (as appropriate), re-analysis for that analyte(s) is required after appropriate dilution. The Contractor must use the least dilution necessary to bring the analyte(s) within the valid analytical range (but not below the CRDL) and report the highest valid value for each analyte as measured from the undiluted and diluted analyses. Unless the Contractor can submit proof that dilution was required to obtain valid results, both diluted and undiluted sample measurements must be contained in the raw data. All sample dilutions shall be made with deionized water appropriately acidified to maintain constant acid strength.

Quality Assurance/Quality Control Measurements: The Contractor is reminded and cautioned that Exhibit D is a compendium of required and/or permitted analytical methods to be used in the performance of analyses under this contract. The quality assurance/quality control procedures or measurements to be performed in association with these methods or analyses are specified in Exhibit E. In the event references to quality assurance measurements in any of the methods appear to be in conflict with or to be less stringent than the requirements of Exhibit E, the requirements of Exhibit E will prevail.

Raw Data Requirements: The Contractor is reminded and cautioned that the collection and provision of raw data may or may not be referred to within the individual methods of Exhibit D or the Quality Assurance Protocol of Exhibit E. The Raw Data Deliverables requirements are specified in Exhibit B, Section II.D.2.d. Raw data collected and provided in association with the performance of analyses under this contract shall conform to the appropriate provisions of Exhibit B.

Glassware Cleaning: Lab glassware to be used in metals analysis must be acid cleaned according to EPA's manual "Methods for Chemical Analysis of Water and Wastes" or an equivalent procedure.

Standard Stock Solutions: Stock solutions to be used for preparing instrument or method calibration standards may be purchased or prepared as described in the individual methods of Exhibit D. All other solutions to be used for Quality Assurance/Quality Control measurements shall conform to the specific requirements of Exhibit E.

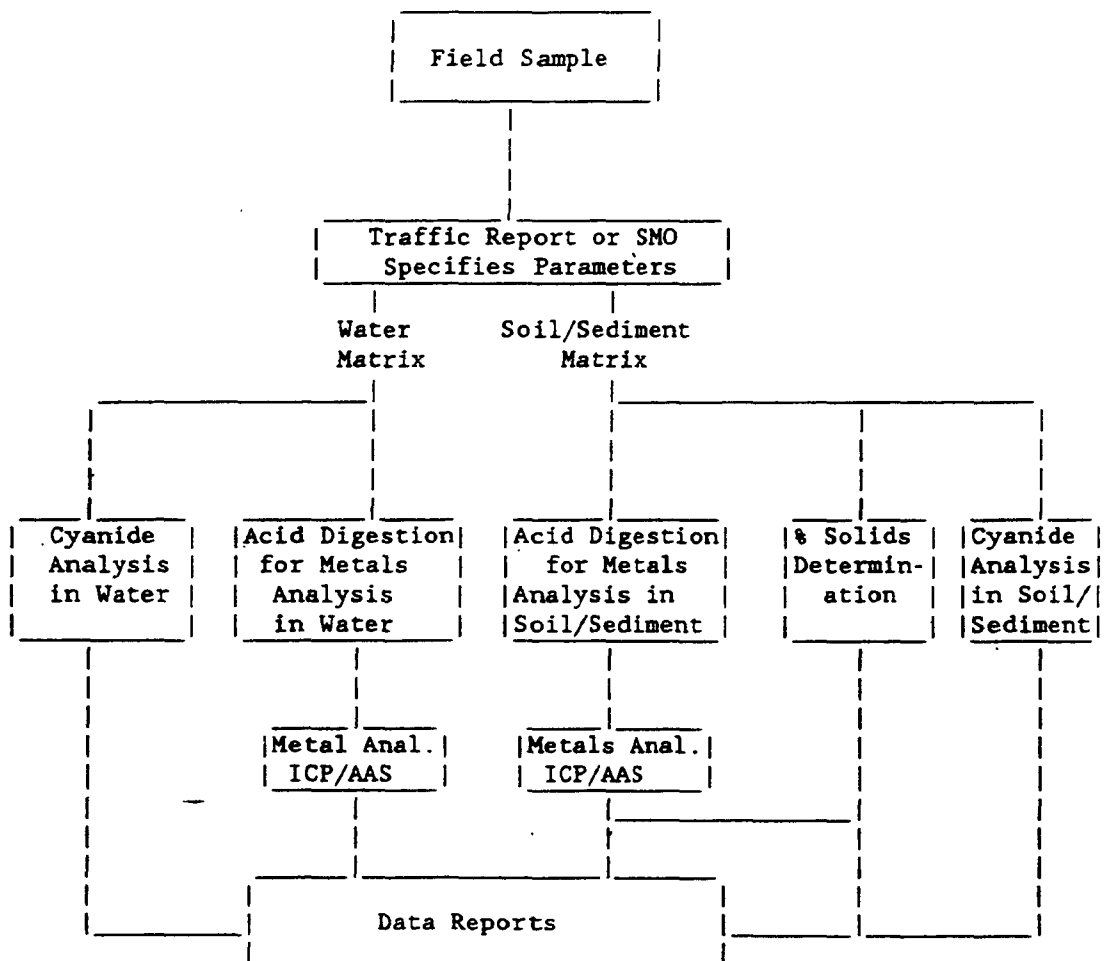
Aqueous Sample pH Measurement: Before sample preparation is initiated on an aqueous sample received in shipment, the Contractor must check the pH of the sample and note in a preparation log if the pH is <2 for a metals sample or if the pH is >12 for a cyanide sample. The Contractor shall not take any pH adjustment action if the sample has not been properly preserved.

Sample Mixing: Unless instructed otherwise by the EPA Project Officer or Deputy Project Officer, all samples shall be mixed thoroughly prior to aliquoting for digestion. No specific procedure is provided herein for homogenization of soil/sediment samples; however, an effort should be made to obtain a representative aliquot.

Background Corrections: Background corrections are required for Flame AA measurements below 350 nm and for all Furnace AA measurements. For ICP background correction requirements, see Exhibit D Section IV, Part A, paragraph 2.1.

Replicate Injections/Exposures: Each furnace analysis requires a minimum of two injection (burns), except for full method of Standard Addition (MSA). All ICP measurements shall require a minimum of two replicate exposures. Appropriate hard copy raw data for each exposure/injection shall be included in the data package in accordance with Exhibit B, Section II, Part D, paragraph 2.d. The average of each set of exposures/injections shall be used for standardization, sample analysis, and reporting as specified in Exhibit D.

Figure 1
INORGANICS METHODS FLOW CHART



SECTION II

SAMPLE PRESERVATION AND HOLDING TIMES

A. Sample Preservation

1. Water Sample Preservation

<u>Measurement Parameter</u>	<u>Container</u> ⁽¹⁾	<u>Preservative</u> ⁽²⁾
Metals ⁽³⁾	P,G	HNO ₃ to pH <2
Cyanide, total and amenable to chlorination	P,G	0.6g ascorbic acid ⁽⁴⁾ NaOH to pH >12 Cool, maintain at 4°C(±2°C) until analysis

FOOTNOTES:

- (1) Polyethylene (P) or glass (G).
- (2) Sample preservation is performed by the sampler immediately upon sample collection.
- (3) Samples are filtered immediately on-site by the sampler before adding preservative for dissolved metals.
- (4) Only used in the presence of residual chlorine.

2. Soil/Sediment Sample Preservation

The preservation required for soil/sediment samples is maintenance at 4°C (± 2°) until analysis.

B. Holding Times for Water and Soil/Sediment Samples

Following are the maximum sample holding times allowable under this contract. To be compliant with this contract, the Contractor must analyze samples within these times even if these times are less than the maximum data submission times allowed in this contract.

<u>Analyte</u>	<u>No. of Days Following Sample Receipt by Contractor</u>
Mercury	26 days
Metals (other than mercury)	180 days
Cyanide	12 days

SECTION III

SAMPLE PREPARATION

A. Water Sample Preparation

1. Acid Digestion Procedure for Furnace Atomic Absorption Analysis

Shake sample and transfer 100 mL of well-mixed sample to a 250-mL beaker, add 1 mL of (1+1) HNO_3 and 2 mL 30% H_2O_2 to the sample. Cover with watch glass or similar cover and heat on a steam bath or hot plate for 2 hours at 95°C or until sample volume is reduced to between 25 and 50 mL, making certain sample does not boil. Cool sample and filter to remove insoluble material. (NOTE: In place of filtering, the sample, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.) Adjust sample volume to 100 mL with deionized distilled water. The sample is now ready for analysis.

Concentrations so determined shall be reported as "total".

If Sb is to be determined by furnace AA, use the digestate prepared for ICP/flame AA analysis.

2. Acid Digestion Procedure for ICP and Flame AA Analyses

Shake sample and transfer 100 mL of well-mixed sample to a 250-mL beaker, add 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HCl to the sample. Cover with watch glass or similar cover and heat on a steam bath or hot plate for 2 hours at 95°C or until sample volume is reduced to between 25 and 50 mL, making certain sample does not boil. Cool sample and filter to remove insoluble material. (NOTE: In place of filtering, the sample, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.) Adjust sample volume to 100 mL with deionized distilled water. The sample is now ready for analysis.

Concentrations so determined shall be reported as "total".

B. Soil/Sediment Sample Preparation

1. Acid Digestion Procedure for ICP, Flame AA and Furnace AA Analyses

a. Scope and Application

This method is an acid digestion procedure used to prepare sediments, sludges, and soil samples for analysis by flame or furnace atomic absorption spectroscopy (AAS) or by inductively coupled plasma spectroscopy (ICP). Samples prepared by this method may be analyzed by AAS or ICP for the following metals:

Aluminum	Chromium	Potassium
Antimony	Cobalt	Selenium
Arsenic	Copper	Silver
Barium	Iron	Sodium
Beryllium	Lead	Thallium
Cadmium	Magnesium	Vanadium
Calcium	Manganese	Zinc
	Nickel	

b. Summary of Method

A representative 1 g (wet weight) sample is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed with either nitric acid or hydrochloric acid. Hydrochloric acid is used as the final reflux acid for the furnace AA analysis of Sb, the flame AA or ICP analysis of Al, Sb, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Ag, Na, Tl, V and Zn. Nitric acid is employed as the final reflux acid for the furnace AA analysis of As, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Ag, Tl, V, and Zn. A separate sample shall be dried for a percent solids determination (Section IV, Part F).

c. Apparatus and Materials

- (1) 250 mL beaker or other appropriate vessel.
- (2) Watch glasses
- (3) Thermometer that covers range of 0° to 200°C
- (4) Whatman No. 42 filter paper or equivalent

d. Reagents

- (1) ASTM Type II water (ASTM D1193): Water must be monitored.
- (2) Concentrated Nitric Acid (sp. gr. 1.41)
- (3) Concentrated Hydrochloric Acid (sp. gr. 1.19)
- (4) Hydrogen Peroxide (30%)

e. Sample Preservation and Handling

Soil/sediment (nonaqueous) samples must be refrigerated at 4°C ($\pm 2^\circ$) from receipt until analysis.

f. Procedure

- (1) Mix the sample thoroughly to achieve homogeneity. For each digestion procedure, weigh (to the nearest 0.01gms) a 1.0 to 1.5 gm portion of sample and transfer to a beaker.
- (2) Add 10 mL of 1:1 nitric acid (HNO_3), mix the slurry, and cover with a watch glass. Heat the sample to 95°C and reflux for 10 minutes without boiling. Allow the sample to cool, add 5 mL of concentrated HNO_3 , replace the watch glass, and reflux for 30 minutes. Do not allow the volume to be reduced to less than 5 mL while maintaining a covering of solution over the bottom of the beaker.
- (3) After the second reflux step has been completed and the sample has cooled, add 2 mL of Type II water and 3 mL of 30% hydrogen peroxide (H_2O_2). Return the beaker to the hot plate for warming to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides, and cool the beaker.
- (4) Continue to add 30% H_2O_2 in 1 mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged. (NOTE: Do not add more than a total of 10 mL 30% H_2O_2 .)
- (5) If the sample is being prepared for the furnace AA analysis of Sb, the flame AA or ICP analysis of Al, Sb, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Ag, Na, Tl, V, and Zn, add 5 mL of 1:1 HCl and 10 mL of Type II water, return the covered beaker to the hot plate, and heat for an additional 10 minutes. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute to 100 mL with Type II water. NOTE: In place of filtering, the sample (after dilution and mixing) may be centrifuged or allowed to settle by gravity overnight to remove insoluble material. The diluted sample has an approximate acid concentration of 2.5% (v/v) HCl and 5% (v/v) HNO_3 . Dilute the digestate 1:1 (200 mL final volume) with acidified water to maintain constant acid strength. The sample is now ready for analysis.
- (6) If the sample is being prepared for the furnace analysis of As, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Ag, Tl, V, and Zn, continue heating the acid-peroxide digestate until the volume has been reduced to approximately 2 mL, add 10 mL of Type II water, and warm the mixture. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute to 100 mL with Type II water (or centrifuge the sample). NOTE: In place of filtering,

the sample (after dilution and mixing) may be centrifuged or allowed to settle by gravity overnight to remove insoluble material. The diluted digestate solution contains approximately 2% (v/v) HNO₃. Dilute the digestate 1:1 (200 mL final volume) with acidified water to maintain constant acid strength. For analysis, withdraw aliquots of appropriate volume, and add any required reagent or matrix modifier. The sample is now ready for analysis.

g. Calculations

- (1) A separate determination of percent solids must be performed (Section IV, Part F).
- (2) The concentrations determined in the digest are to be reported on the basis of the dry weight of the sample.

$$\text{Concentration (dry wt.) (mg/kg)} = \frac{C \times V}{W \times S}$$

Where,

- C = Concentration (mg/L)
- V = Final volume in liters after sample preparation
- W = Weight in kg of wet sample
- S = % Solids/100

h. Bibliography

Modification (by committee) of Method 3050, SW-846, 2nd ed., Test Methods for Evaluating Solid Waste, EPA Office of Solid Waste and Emergency Response, July 1982.

SECTION IV

SAMPLE ANALYSIS

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PART A - INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRIC METHOD⁺

Method 200.7 CLP-M*
INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRIC METHOD
FOR TRACE ELEMENT ANALYSIS OF WATER AND WASTES

1. Scope and Application

- 1.1 Dissolved elements are determined in filtered and acidified samples. Appropriate steps must be taken in all analyses to ensure that potential interferences are taken into account. This is especially true when dissolved solids exceed 1500 mg/L. (See 5.)
- 1.2 Total elements are determined after appropriate digestion procedures are performed. Since digestion techniques increase the dissolved solids content of the samples, appropriate steps must be taken to correct for potential interference effects. (See 5.)
- 1.3 Table 1 lists elements along with recommended wavelengths and typical estimated instrumental detection limits using conventional pneumatic nebulization. Actual working detected limits are sample dependent and as the sample matrix varies, these concentrations may also vary. In time, other elements may be added as more information becomes available and as required.
- 1.4 Because of the differences between various makes and models of satisfactory instruments, no detailed instrumental operating instructions can be provided. Instead, the analyst is referred to the instructions provided by the manufacturer of the particular instrument.

2. Summary of Method

- 2.1 The method describes a technique for the simultaneous or sequential multielement determination of trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the line are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or

⁺A bibliography citing method references appears in paragraph 11 of the method.

*CLP-M modified for the Contract Laboratory Program.

both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in 5.1 (and tests for their presence as described in 5.2) should also be recognized and appropriate corrections made.

3. Definitions

- 3.1 Dissolved -- Those elements which will pass through a 0.45 μ m membrane filter.
- 3.2 Suspended -- Those elements which are retained by a 0.45 μ m membrane filter.
- 3.3 Total -- The concentration determined on an unfiltered sample following vigorous digestion.
- 3.4 Instrumental detection limits -- See Exhibit E.
- 3.5 Sensitivity -- The slope of the analytical curve, i.e. functional relationship between emission intensity and concentration.
- 3.6 Instrument check standard -- A multi-element standard of known concentrations prepared by the analyst to monitor and verify instrument performance on a daily basis. (See 7.6.1.)
- 3.7 Interference check sample -- A solution containing both interfering and analyte elements of known concentration that can be used to verify background and interelement correction factors. (See 7.6.2.)
- 3.8 Quality control sample -- A solution obtained from an outside source having known concentration values to be used to verify the calibration standards. (See 7.6.3.)
- 3.9 Calibration standards -- A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve). (See 7.4.)
- 3.10 Linear dynamic range -- The concentration range over which the analytical curve remains linear as determined in Exhibit E.
- 3.11 Reagent blank -- A volume of deionized, distilled water containing the same acid matrix as the calibration standards carried through the entire analytical scheme. (See 7.5.2.)
- 3.12 Calibration blank -- A volume of deionized, distilled water acidified with HNO_3 and HCl . (See 7.5.1.)

- 3.13 Method of standard addition -- The standard addition technique involves the use of the unknown and the unknown-plus-a-known amount of standard by adding known amounts of standard to one or more aliquots of the processed sample solution.

4. Safety

- 4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material handling data sheets should be made available to all personnel involved in the chemical analysis.

5. Interferences

- 5.1 Several types of interference effects may contribute to inaccuracies in the determination of trace elements. They can be summarized as follows:

- 5.1.1 Spectral interferences can be categorized as 1) overlap of a spectral line from another element; 2) unresolved overlap of molecular band spectra; 3) background contribution from continuous or recombination phenomena; and 4) background contribution from stray light from the line emission of high concentration elements. The first of these effects can be compensated by utilizing a computer correction of the raw data, requiring the monitoring and measurement of the interfering element. The second effect may require selection of an alternate wavelength. The third and fourth effects can usually be compensated by a background correction adjacent to the analyte line. In addition, users of simultaneous multi-element instrumentation must assume the responsibility of verifying the absence of spectral interference from an element that could occur in a sample but for which there is no channel in the instrument array.

Listed in Table 2 are some interference effects for the recommended wavelengths given in Table 1. The data in Table 2 are intended for use only as a rudimentary guide for the indication of potential spectral interferences. For this purpose, linear relations between concentration and intensity for the analytes and the interferents can be assumed. The interference information, which was collected at the Ames Laboratory**, is expressed as analyte concentration equivalents (i.e., false analyte concentrations) arising from 100 mg/L of the interferent element.

**Ames Laboratory, USDOE, Iowa State University, Ames, Iowa 50011.

The suggested use of this information is as follows: Assume that arsenic (at 193.696 nm) is to be determined in a sample containing approximately 10 mg/L of aluminum. According to Table 2, 100 mg/L of aluminum would yield a false signal for arsenic equivalent to approximately 1.3 mg/L. Therefore, 10 mg/L of aluminum would result in a false signal for arsenic equivalent to approximately 0.13 mg/L. The reader is cautioned that other analytical systems may exhibit somewhat different levels of interference than those shown in Table 2, and that the interference effects must be evaluated for each individual system. Only those interferents listed were investigated and the blank spaces in Table 2 indicate that measurable interferences were not observed from the interferent concentrations listed in Table 3. Generally, interferences were discernible if they produced peaks or background shifts corresponding to 2-5% of the peaks generated by the analyte concentrations also listed in Table 3.

At present, information on the listed silver and potassium wavelengths are not available but it has been reported that second order energy from the magnesium 383.231 nm wavelength interferes with the listed potassium line at 766.491 nm.

- 5.1.2 Physical interferences are generally considered to be effects associated with the sample nebulization and transport processes. Such properties as change in viscosity and surface tension can cause significant inaccuracies especially in samples which may contain high dissolved solids and/or acid concentrations. The use of a peristaltic pump may lessen these interferences. If these types of interferences are operative, they must be reduced by dilution of the sample and/or utilization of standard addition techniques. Another problem which can occur from high dissolved solids is salt buildup at the tip of the nebulizer. This affects aerosol flow rate causing instrumental drift.

Wetting the argon prior to nebulization, the use of a tip washer, or sample dilution have been used to control this problem. Also, it has been reported that better control of the argon flow rate improves instrument performance. This is accomplished with the use of mass flow controllers.

- 5.1.3 Chemical interferences are characterized by molecular compound formation, ionization effects and solute vaporization effects. Normally these effects are not pronounced with the ICP technique, however, if observed they can be minimized by careful selection of operating conditions (that is, incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. These types of interferences can be highly dependent on matrix type and the specific analyte element.

- 5.2 Prior to reporting concentration data for the analyte elements, the Contractor must analyze and report the results of the ICP Serial Dilution Analysis. The ICP Serial Dilution Analysis must be performed on a sample from each group of samples of a similar matrix type (i.e., water, soil) and concentration (i.e., low, medium) or for each Sample Delivery Group, whichever is more frequent. Samples identified as field blanks cannot be used for Serial Dilution Analysis.

If the analyte concentration is sufficiently high (minimally a factor of 50 above the instrumental detection limit in the original sample), the serial dilution (a five fold dilution) must then agree within 10% of the original determination after correction for dilution. If the dilution analysis for one or more analytes is not within 10%, a chemical or physical interference effect must be suspected, and the data for all affected analytes in the samples received associated with that serial dilution must be flagged with an "E" on FORM IX-IN and FORM I-IN.

6. Apparatus

6.1 Inductively Coupled Plasma-Atomic Emission Spectrometer

6.1.1 Computer controlled atomic emission spectrometer with background correction.

6.1.2 Radio frequency generator.

6.1.3 Argon gas supply, welding grade or better.

- 6.2 Operating conditions -- Because of the differences between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of the particular instrument. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be investigated and established for each individual analyte line on that particular instrument. All measurements must be within the instrument linear range where correction factors are valid. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions used satisfy the analytical requirements and to maintain quality control data confirming instrument performance and analytical results.

7. Reagents and Standards

- 7.1 Acids used in the preparation of standards and for sample processing must be ultra-high purity grade or equivalent. Redistilled acids are acceptable.

7.1.1 Acetic acid, conc. (sp gr 1.06)

7.1.2 Hydrochloric acid, conc. (sp gr 1.19).

7.1.3 Hydrochloric acid, (1+1): Add 500 mL conc. HCl (sp gr 1.19) to 400 mL deionized, distilled water and dilute to 1 liter

- 7.1.4 Nitric acid, conc. (sp gr 1.41).
- 7.1.5 Nitric acid, (1+1): Add 500 mL conc. HNO_3 (sp gr 1.41) to 400 mL deionized, distilled water and dilute to 1 liter.
- 7.2 Deionized, distilled water: Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use deionized, distilled water for the preparation of all reagents, calibration standards and as dilution water. The purity of this water must be equivalent to ASTM Type II reagent water of Specification D 1193.
- 7.3 Standard stock solutions may be purchased or prepared from ultra high purity grade chemicals or metals. All salts must be dried for 1 hour at 105° unless otherwise specified.
- (CAUTION: Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.) Typical stock solution preparation procedures follow:
- 7.3.1 Aluminum solution, stock, 1 mL = 100 ug Al: Dissolved 0.100 g of aluminum metal in an acid mixture of 4 mL of (1+1) HCl and 1 mL of conc. HNO_3 in a beaker. Warm gently to effect solution. When solution is complete, transfer quantitatively to a liter flask, add an additional 10 mL of (1+1) HCl and dilute to 1000 mL with deionized, distilled water.
- 7.3.2 Antimony solution stock, 1 mL = 100 ug Sb: Dissolve 0.2669 g $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6$ in deionized distilled water, add 10 mL (1+1) HCl and dilute to 1000 mL with deionized, distilled water.
- 7.3.3 Arsenic solution, stock, 1 mL = 100 ug As: Dissolve 0.1320 g of As_2O_3 in 100 mL of deionized, distilled water containing 0.4 g NaOH. Acidify the solution with 2 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.
- 7.3.4 Barium solution, stock, 1 mL = 100 ug Ba: Dissolve 0.1516 g BaCl_2 (dried at 250°C for 2 hrs) in 10 mL deionized, distilled water with 1 mL (1+1) HCl. Add 10.0 mL (1+1) HCl and dilute to 1,000 mL with deionized, distilled water.
- 7.3.5 Beryllium solution, stock, 1 mL = 100 ug Be: Do not dry. Dissolve 1.966 g $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$, in deionized, distilled water, add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.
- 7.3.6 Boron solution, stock, 1 mL = 100 ug B: Do not dry. Dissolve 0.5716 g anhydrous H_3BO_3 in deionized, distilled water and dilute to 1,000 mL. Use a reagent meeting ACS specifications, keep the bottle tightly stoppered and store in a desiccator to prevent the entrance of atmospheric moisture.

- 7.3.7 Cadmium solution, stock, 1 mL = 100 ug Cd: Dissolve 0.1142 g CdO in a minimum amount of (1+1) HNO₃. Heat to increase rate of dissolution. Add 10.0 mL conc. HNO₃ and dilute to 1,000 mL with deionized, distilled water.
- 7.3.8 Calcium solution, stock, 1 mL = 100 ug Ca: Suspend 0.2498 g CaCO₃ dried at 180°C for 1 h before weighing in deionized, distilled water and dissolve cautiously with a minimum amount of (1+1) HNO₃. Add 10.0 mL conc. HNO₃ and dilute to 1,000 mL with deionized, distilled water.
- 7.3.9 Chromium solution, stock, 1 mL = 100 ug Cr: Dissolve 0.1923 g of CrO₃ in deionized, distilled water. When solution is complete acidify with 10 mL conc. HNO₃ and dilute to 1,000 mL with deionized, distilled water.
- 7.3.10 Cobalt solution stock, 1 mL = 100 ug Co: Dissolve 0.1000 g of cobalt metal in a minimum amount of (1+1) HNO₃. Add 10.0 mL (1+1) HCl and dilute to 1,000 mL with deionized, distilled water.
- 7.3.11 Copper solution, stock, 1 mL = 100 ug Cu: Dissolve 0.1252 g CuO in a minimum amount of (1+1) HNO₃. Add 10.0 mL conc. HNO₃ and dilute to 1,000 mL with deionized, distilled water.
- 7.3.12 Iron solution, stock, 1 mL = 100 ug Fe: Dissolve 0.1430 g Fe₂O₃ in a warm mixture of 20 mL (1+1) HCl and 2 mL of conc. HNO₃. Cool, add an additional 5 mL of conc. HNO₃ and dilute to 1,000 mL with deionized, distilled water.
- 7.3.13 Lead solution, stock, 1 mL = 100 ug Pb: Dissolve 0.1599 g Pb(NO₃)₂ in a minimum amount of (1+1) HNO₃. Add 10.0 mL of conc. HNO₃ and dilute to 1,000 mL with deionized, distilled water.
- 7.3.14 Magnesium solution, stock, 1 mL = 100 ug Mg: Dissolve 0.1658 g MgO in a minimum amount of (1+1) HNO₃. Add 10.0 mL conc. HNO₃ and dilute to 1,000 mL with deionized, distilled water.
- 7.3.15 Manganese solution, stock, 1 mL = 100 ug Mn: Dissolve 0.1000 g of manganese metal in the acid mixture, 10 mL conc. HCl and 1 mL conc. HNO₃, and dilute to 1,000 mL with deionized, distilled water.
- 7.3.16 Molybdenum solution, stock, 1 mL = 100 ug Mo: Dissolve 0.2043 g (NH₄)₂MoO₄ in deionized, distilled water and dilute to 1,000 mL.
- 7.3.17 Nickel solution, stock, 1 mL = 100 ug Ni: Dissolve 0.1000 g of nickel metal in 10 mL hot conc. HNO₃, cool and dilute to 1,000 mL with deionized, distilled water.

- 7.3.18 Potassium solution, stock, 1 mL = 100 ug K: Dissolve 0.1907 g KCl, dried at 110°C, in deionized, distilled water. Dilute to 1,000 mL.
- 7.3.19 Selenium solution, stock, 1 mL = 100 ug Se: Do not dry. Dissolve 0.1727 g H_2SeO_3 (actual assay 94.6%) in deionized, distilled water and dilute to 1,000 mL.
- 7.3.20 Silica solution, stock, 1 mL = 100 ug SiO_2 : Do not dry. Dissolve 0.4730 g $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ in deionized, distilled water. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.
- 7.3.21 Silver solution, stock, 1 mL = 100 ug Ag: Dissolve 0.1575 g AgNO_3 in 100 mL of deionized, distilled water and 10 mL conc. HNO_3 . Dilute to 1,000 mL with deionized, distilled water.
- 7.3.22 Sodium solution, stock, 1 mL = 100 ug Na: Dissolve 0.2542 g NaCl in deionized, distilled water. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.
- 7.3.23 Thallium solution, stock, 1 mL = 100 ug Tl: Dissolve 0.1303 g TlNO_3 in deionized, distilled water. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.
- 7.3.24 Vanadium solution, stock, 1 mL = 100 ug V: Dissolve 0.2297 NH_4VO_3 in a minimum amount of conc. HNO_3 . Heat to increase rate of dissolution. Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.
- 7.3.25 Zinc solution, stock, 1 mL = 100 ug Zn: Dissolve 0.1245 g ZnO in a minimum amount of dilute HNO_3 . Add 10.0 mL conc. HNO_3 and dilute to 1,000 mL with deionized, distilled water.
- 7.4 Mixed calibration standard solutions -- Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks. (See 7.4.1 thru 7.4.5.) Add 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HCl and dilute to 100 mL with deionized, distilled water. (See NOTE in 7.4.5) Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standard solutions to a FEP fluorocarbon or unused polyethylene bottle for storage. Fresh mixed standards should be prepared as needed with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample and monitored weekly for stability (see 7.6.3). Although not specifically required, some typical calibration standard combinations follow when using those specific wavelengths listed in Table 1.
- 7.4.1 Mixed standard solution I -- Manganese, beryllium, cadmium, lead, and zinc.

- 7.4.2 Mixed standard solution II -- Barium, copper, iron, vanadium, and cobalt.
 - 7.4.3 Mixed standard solution III -- Molybdenum, silica, arsenic, and selenium.
 - 7.4.4 Mixed standard solution IV -- Calcium, sodium, potassium, aluminum, chromium and nickel.
 - 7.4.5 Mixed standard solution V -- Antimony, boron, magnesium, silver, and thallium.
- NOTE: If the addition of silver to the recommended acid combination results in an initial precipitation add 15 mL of deionized distilled water and warm the flask until the solution clears. Cool and dilute to 100 mL with deionized, distilled water. For this acid combination the silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap water matrix for 30 days. Higher concentrations of silver require additional HCl.
- 7.5 Two types of blanks are required for the analysis. The calibration blank (3.13) is used in establishing the analytical curve while the reagent blank (preparation blank, 3.12) is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.
 - 7.5.1 The calibration blank is prepared by diluting 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HCl to 100 mL with deionized, distilled water. Prepare a sufficient quantity to be used to flush the system between standards and samples.
 - 7.5.2 The reagent blank (or preparation blank - See Exhibit E) must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.
 - 7.6 In addition the calibration standards, an instrument check standard (3.6), an interference check sample (3.7) and a quality control sample (3.8) are also required for the analyses.
 - 7.6.1 The instrument check standard for continuing calibration verification is prepared by the analyst by combining compatible elements at a concentration equivalent to the mid-points of their respective calibration curves. (See 10.1.3.)
 - 7.6.2 The interference check sample is prepared by the analyst, or obtained from EPA if available (Exhibit E).

- 7.6.3 The quality control sample for the initial calibration verification should be prepared in the same acid matrix as the calibration standards and in accordance with the instructions provided by the supplier. EPA will either supply a quality control sample or information where one of equal quality can be procured. (See 10.1.1.)

8. Procedure

- 8.1 Set up instrument with proper operating parameters established in Section 6.2. The instrument must be allowed to become thermally stable before beginning. This usually requires at least 30 min. of operation prior to calibration.
- 8.2 Initiate appropriate operating configuration of computer.
- 8.3 Profile and calibrate instrument according to instrument manufacturer's recommended procedures, using mixed calibration standard solutions such as those described in Section 7.4. Flush the system with the calibration blank (7.5.1) between each standard. (NOTE: For boron concentrations greater than 500 ug/L extended flush times of 1 to 2 minutes may be required.)
- 8.4 Begin the sample run flushing the system with the calibration blank solution (7.5.1) between each sample. (See NOTE in 8.3.) Analyze the instrument check standard (7.6.1) and the calibration blank (7.5.1) each 10 analytical samples.
- 8.5 A minimum of two replicate exposures are required for standardization and all QC and sample analyses. The average result of the multiple exposures for the standardization and all QC and sample analyses shall be used.

9. Calculation

- 9.1 Reagent blanks (preparation blanks) should be treated as specified in Exhibit E.
- 9.2 If dilutions were performed, the appropriate factor must be applied to sample values.
- 9.3 Units must be clearly specified.

10. Quality Control (Instrumental)

- 10.1 Quality control must be performed as specified in Exhibit E.

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TABLE 1 - RECOMMENDED WAVELENGTHS(2) AND ESTIMATED
INSTRUMENTAL DETECTION LIMITS

Element	Wavelength, nm(1)	Estimated Detection Limit, ug/L(2)
Aluminum	308.215	45
Antimony	206.833	32
Arsenic	193.696	53
Barium	455.403	2
Beryllium	313.042	0.3
Boron	249.773	5
Cadmium	226.502	4
Calcium	317.933	10
Chromium	267.716	7
Cobalt	228.616	7
Copper	324.754	6
Iron	259.940	7
Lead	220.353	42
Magnesium	279.079	30
Manganese	257.610	2
Molybdenum	202.030	8
Nickel	231.604	15
Potassium	766.491	See(3)
Selenium	196.026	75
Silica (SiO ₂)	288.158	58
Silver	328.068	7
Sodium	588.995	29
Thallium	190.864	40
Vanadium	292.402	8
Zinc	213.856	2

- (1) The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference. (See 5.1.1). The use of alternate wavelengths must be reported (in nm) with the sample data.
- (2) The estimated instrumental detection limits as shown are taken from "Inductively Coupled Plasma-Atomic Emission Spectroscopy-Prominent Lines," EPA-600/4-79-017. They are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.
- (3) Highly dependent on operating conditions and plasma position.

TABLE 2. EXAMPLE OF ANALYTE CONCENTRATION EQUIVALENTS (MG/L) ARISING FROM INTERFERENTS AT THE 100 MG/L LEVEL

Analyte	Wavelength, nm	Interferent									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Ti	V
Aluminum	308.215	--	--	--	--	--	--	0.21	--	--	1.4
Antimony	206.833	0.47	--	2.9	--	0.08	--	--	--	.25	0.45
Arsenic	193.696	1.3	--	0.44	--	--	--	--	--	--	1.1
Barium	455.403	--	--	--	--	--	--	--	--	--	--
Beryllium	313.042	--	--	--	--	--	--	--	--	0.04	0.05
Boron	249.773	0.04	--	--	--	0.32	--	--	--	--	--
Cadmium	226.502	--	--	--	--	0.03	--	--	0.02	--	--
Calcium	317.933	--	--	0.08	--	0.01	0.01	0.04	--	0.03	0.03
Chromium	267.716	--	--	--	--	0.003	--	0.04	--	--	0.04
Cobalt	228.616	--	--	0.03	--	0.005	--	--	0.03	0.15	--
Copper	324.754	--	--	--	--	0.003	--	--	--	0.05	0.02
Iron	259.940	--	--	--	--	--	--	0.12	--	--	--
Lead	220.353	0.17	--	--	--	--	--	--	--	--	--
Magnesium	279.079	--	0.02	0.11	--	0.13	--	0.25	--	0.07	0.12
Manganese	257.610	0.005	--	0.01	--	0.002	0.002	--	--	--	--
Molybdenum	202.030	0.05	--	--	--	0.03	--	--	--	--	--
Nickel	231.604	--	--	--	--	--	--	--	--	--	--
Selenium	196.026	0.23	--	--	--	0.09	--	--	--	--	--
Silicon	288.158	--	--	0.07	--	--	--	--	--	--	0.01
Sodium	588.995	--	--	--	--	--	--	--	--	0.08	--
Thallium	190.864	0.30	--	--	--	--	--	--	--	--	--
Vanadium	292.402	--	--	0.05	--	0.005	--	--	--	0.02	--
Zinc	213.856	--	--	--	0.14	--	--	--	0.29	--	--

TABLE 3. INTERFERENT AND ANALYTE ELEMENTAL CONCENTRATIONS USED
FOR INTERFERENCE MEASUREMENTS IN TABLE 2

Analytes	(mg/L)	Interferents	(mg/L)
Al	10	Al	1000
As	10	Ca	1000
B	10	Cr	200
Ba	1	Cu	200
Be	1	Fe	1000
Ca	1	Mg	1000
Cd	10	Mn	200
Co	1	Ni	200
Cr	1	Ti	200
Cu	1	V	200
Fe	1		
Mg	1		
Mn	1		
Mo	10		
Na	10		
Ni	10		
Pb	10		
Sb	10		
Se	10		
Si	1		
Tl	10		
V	1		
Zn	10		

PART B - ATOMIC ABSORPTION METHODS, FURNACE TECHNIQUE⁺

<u>Analyte/Method</u>	<u>Page No.</u>
Antimony - Method 204.2 CLP-M*	D-25
Arsenic - Method 206.2 CLP-M	D-26
Beryllium - Method 210.2 CLP-M	D-28
Cadmium - Method 213.2 CLP-M	D-29
Chromium - Method 218.2 CLP-M	D-30
Lead - Method 239.2 CLP-M	D-31
Selenium - Method 270.2 CLP-M	D-33
Silver - Method 272.2 CLP-M	D-35
Thallium - Method 279.2 CLP-M	D-36

⁺From "Methods for Chemical Analysis of Water and Wastes" (EPA-600/4-79-020), Metals-4, as modified for use in the Contract Laboratory Program).

*CLP-M modified for the Contract Laboratory Program.

ANTIMONY

Method 204.2 CLP-M* (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 20-300 ug/L

Approximate Detection Limit: 3 ug/L

Preparation of Standard Solution

1. Stock solution: Carefully weigh 2.7426 g of antimony potassium tartrate (analytical reagent grade) and dissolve in deionized distilled water. Dilute to 1 Liter with deionized water. 1 mL = 1 mg Sb (1000 mg/L).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C.
2. Ashing Time and Temp: 30 sec @ 800°C.
3. Atomizing Time and Temp: 10 sec @ 2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 217.6 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required.
3. Nitrogen may also be used as the purge gas.
4. If chloride concentration presents a matrix problem or causes a loss previous to atomization, add an excess 5 mg of ammonium nitrate to the furnace and ash using a ramp accessory or with incremental steps until the recommended ashing temperature is reached.
5. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
6. If method of standard addition is required, follow the procedure given in Exhibit E.

*CLP-M modified for the Contract Laboratory Program.

ARSENIC

Method 206.2 CLP-M* (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 5-100 ug/L

Approximate Detection Limit: 1 ug/L

Preparation of Standard Solution

1. Stock solution: Dissolve 1.320 g of arsenic trioxide, As_2O_3 (analytical reagent grade) in 100 mL of deionized distilled water containing 4 g NaOH. Acidify the solution with 20 mL conc. HNO_3 and dilute to 1 Liter. 1 mL = 1 mg As (1000 mg/l).
2. Nickel Nitrate Solution, 5%: Dissolve 24.780 g of ACS reagent grade $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in deionized distilled water and make up to 100 mL.
3. Nickel Nitrate Solution, 1%: Dilute 20 mL of the 5% nickel nitrate to 100 mL with deionized distilled water.
4. Working Arsenic Solution: Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Withdraw appropriate aliquots of the stock solution, add 1 mL of conc. HNO_3 , 2 mL of 30% H_2O_2 and 2 mL of the 5% nickel nitrate solution. Dilute to 100 mL with deionized distilled water.

Sample Preparation

1. Add 100 uL of the 5% nickel nitrate solution to 5 mL of the digested sample. The sample is now ready for injection into the furnace.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C.
2. Ashing Time and Temp: 30 sec @ 1100°C.
3. Atomizing Time and Temp: 10 sec @ 2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 193.7 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, purge gas interrupt and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required. Background correction made by the deuterium arc method does not adequately compensate for high levels of certain interferents (ie., Al, Fe). If conditions occur where significant interference is suspected, the lab must switch to an alternate wavelength or take other appropriate actions to compensate for the interference effects.
3. For every sample analyzed, verification is necessary to determine that

*CLP-M modified for the Contract Laboratory Program.

method of standard addition is not required (see Exhibit E).

4. If method of standard addition is required, follow the procedure given in Exhibit E).
5. The use of the Electrodeless Discharge Lamps (EDL) for the light source is recommended.

BERYLLIUM

Method 210.2 CLP-M* (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 1-30 ug/L

Approximate Detection Limit: 0.2 ug/L

Preparation of Standard Solution

1. Stock solution: Dissolve 11.6586g of beryllium sulfate, BeSO_4 , in deionized distilled water containing 2 mL concentrated nitric acid and dilute to 1 Liter. 1 mL = 1 mg Be (1000 mg/L).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C.
2. Ashing Time and Temp: 30 sec @ 1000°C.
3. Atomizing Time and Temp: 10 sec @ 2800°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 234.9 nm
6. The operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required.
3. Because of possible chemical interaction, nitrogen should not be used as a purge gas.
4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E)
5. If method of standard addition is required, follow the procedure given in Exhibit E.

*CLP-M modified for the Contract Laboratory Program.

CADMIUM

Method 213.2 CLP-M* (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 0.5-10 ug/L

Approximate Detection Limit: 0.1 ug/L

Preparation of Standard Solution

1. Stock solution: Carefully weigh 2.282g of cadmium sulfate, $3 \text{ CdSO}_4 \cdot 8 \text{ H}_2\text{O}$ (analytical reagent grade) and dissolve in deionized distilled water. Make up to 1 Liter with deionized distilled water. 1 mL = 1 mg Cd (1000 mg/L).
2. Ammonium Phosphate solution (40%): Dissolve 40 grams of ammonium phosphate, $(\text{NH}_4)_2\text{HPO}_4$ (analytical reagent grade) in deionized distilled water and dilute to 100 mL.
3. Prepare dilutions of stock cadmium solution to be used as calibration standards at the time of analysis. To each 100 mL of standard and sample alike add 2.0 mL of the ammonium phosphate solution. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C.
2. Ashing Time and Temp: 30 sec @ 500°C.
3. Atomizing Time and Temp: 10 sec @ 1900°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 228.8 nm
6. The operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required.
3. Contamination from the work area is critical in cadmium analysis. Use pipette tips which are free of cadmium.
4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
5. If method of standard addition is required, follow the procedure given in Exhibit E.

*CLP-M modified for the Contract Laboratory Program.

CHROMIUM

Method 218.2 CLP-M* (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 5-100 ug/L

Approximate Detection Limit: 1 ug/L

Preparation of Standard Solution

1. Stock solution: Prepare as described under Part C methods, AA Flame Technique.
2. Calcium Nitrate solution: Dissolve 11.8 grams of calcium nitrate, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (analytical reagent grade) in deionized distilled water and dilute to 100 mL. 1 mL = 20 mg Ca.
3. Prepare dilutions of the stock chromium solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation. To each 100 mL of standard and sample alike, add 1 mL of 30% H_2O_2 and 1 mL of the calcium nitrate solution.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C.
2. Ashing Time and Temp: 30 sec @ 1000°C.
3. Atomizing Time and Temp: 10 sec @ 2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 357.9 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only.
2. Hydrogen peroxide is added to the acidified solution to convert all chromium to the trivalent state. Calcium is added to a level above 200 mg/L where its suppressive effect becomes constant up to 1000 mg/L.
3. Background correction is required.
4. Nitrogen should not be used as a purge gas because of possible CN band interference.
5. Pipette tips have been reported to be a possible source of contamination.
6. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
7. If method of standard addition is required, follow the procedure given in Exhibit E.

*CLP-M modified for the Contract Laboratory Program.

LEAD

Method 239.2 CLP-M* (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 5-100 ug/L

Approximate Detection Limit: 1 ug/L

Preparation of Standard Solution

1. Stock solution: Carefully weigh 1.599 g of lead nitrate, $\text{Pb}(\text{NO}_3)_2$ (analytical reagent grade), and dissolve in deionized distilled water. When solution is complete, acidify with 10 mL redistilled HNO_3 and dilute to 1 Liter with deionized distilled water. 1 mL = 1 mg Pb (1000mg/L).
2. Lanthanum Nitrate solution: Dissolve 58.64 g of ACS reagent grade La_2O_3 in 100 mL conc. HNO_3 and dilute to 1000 mL with deionized distilled water. 1 mL = 50 mg La.
3. Working Lead solution: Prepare dilutions of stock lead solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation. To each 100 mL of diluted standard add 10 mL of the lanthanum nitrate solution.

Sample Preparation

1. To each 100 mL of prepared sample solution add 10 mL of the lanthanum nitrate solution.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C.
2. Ashing Time and Temp: 30 sec @ 500°C.
3. Atomizing Time and Temp: 10 sec @ 2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 283.3 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required.

*CLP-M modified for the Contract Laboratory Program.

3. Greater sensitivity can be achieved using the 217.0 nm line, but the optimum concentration range is reduced. The use of a lead electrodeless discharge lamp at this lower wavelength has been found to be advantageous. Also a lower atomization temperature (2400°C) may be preferred.
4. To suppress sulfate interference (up to 1500 ppm) lanthanum is added as the nitrate to both samples and calibration standards. (Atomic Absorption Newsletter Vol. 15, No. 3, p. 71, May-June 1976).
5. Since glassware contamination is a severe problem in lead analysis, all glassware should be cleaned immediately prior to use, and once cleaned, should not be open to the atmosphere except when necessary.
6. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
7. If method of standard addition is required, follow the procedure given in Exhibit E.

SELENIUM

Method 270.2 CLP-M* (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 5-100 ug/L

Approximate Detection Limit: 2 ug/L

Preparation of Standard Solution

1. Stock Selenium solution: Dissolve 0.3453 g of selenous acid (actual assay 94.6% H_2SeO_3) in deionized distilled water and make up to 200 mL. 1 mL = 1 mg Se (1000 mg/L).
2. Nickel Nitrate solution, 5%: Dissolve 24.780 g of ACS reagent grade $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in deionized distilled water and make up to 100 mL.
3. Nickel Nitrate solution, 1%: Dilute 20 mL of the 5% nickel nitrate to 100 mL with deionized distilled water.
4. Working Selenium solution: Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation. Withdraw appropriate aliquots of the stock solution, add 1 mL of conc. HNO_3 , 2 mL of 30% H_2O_2 and 2 mL of the 5% nickel nitrate solution. Dilute to 100 mL with deionized distilled water.

Sample Preparation

1. Add 100 uL of the 5% nickel nitrate solution to 5 mL of the digested sample. The sample is now ready for injection into the furnace.

Instrument Parameters

1. Drying Time and Temp: 30 sec @ 125°C.
2. Charring Time and Temp: 30 sec @ 1200°C.
3. Atomizing Time and Temp: 10 sec @ 2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 196.0 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, purge gas interrupt and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required. Background correction made by the deuterium arc method does not adequately compensate for high levels of certain interferents (i.e., Al, Fe). If conditions

*CLP-M modified for the Contract Laboratory Program.

occur where significant interference is suspected, the lab must switch to an alternate wavelength or take other appropriate actions to compensate for the interference effects.

3. Selenium analysis suffers interference from chlorides (>800 mg/L) and sulfate (>200 mg/L). For the analysis of industrial effluents and samples with concentrations of sulfate from 200 to 2000 mg/L, both samples and standards should be prepared to contain 1% nickel.
4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
5. If method of standard addition is required, follow the procedure given in Exhibit E.
6. The use of the Electrodeless Discharge Lamp (EDL) for the light source is recommended.

SILVER

Method 272.2 CLP-M* (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 1-25 ug/L

Approximate Detection Limit: 0.2 ug/L

Preparation of Standard Solution

1. Stock solution: Dissolve 1.575 g of AgNO_3 (analytical reagent grade) in deionized distilled water. Add 10 mL of concentrated HNO_3 and make up to 1 Liter. 1 mL = 1 mg Ag (1000 mg/L).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C.
2. Ashing Time and Temp: 30 sec @ 400°C.
3. Atomizing Time and Temp: 10 sec @ 2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 328.1 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required.
3. The use of halide acids should be avoided.
4. If absorption to container walls or formation of AgCl is suspected, see Part G, AA methods Flame Technique.
5. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
6. If method of standard addition is required, follow the procedure given in Exhibit E.

*CLP-M modified for the Contract Laboratory Program.

THALLIUM

Method 279.2 CLP-M* (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 5-100 ug/L

Approximate Detection Limit: 1 ug/L

Preparation of Standard Solution

1. Stock solution: Dissolve 1.303g of thallium nitrate, $TlNO_3$ (analytical reagent grade) in deionized distilled water. Add 10 mL of concentrated nitric acid and dilute to 1 Liter with deionized distilled water. 1 mL = 1 mg Tl (1000 mg/L).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C.
2. Ashing Time and Temp: 30 sec @ 400°C.
3. Atomizing Time and Temp: 10 sec @ 2400°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 276.8 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required.
3. Nitrogen may also be used as the purge gas.
4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
5. If method of standard addition is required, follow the procedure given in Exhibit E.

*CLP-M modified for the Contract Laboratory Program.

PART C - ATOMIC ABSORPTION METHODS, FLAME TECHNIQUE⁺

<u>Analyte/Method</u>	<u>Page No.</u>
Calcium - Method 215.1 CLP-M*	D-38
Magnesium - Method 242.1 CLP-M	D-39
Potassium - Method 258.1 CLP-M	D-40
Sodium - Method 273.1 CLP-M	D-41

⁺From "Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue", USEPA EMSL, Cincinnati, Ohio, August 1977, Revised October 1980, as modified for use in the Contract Laboratory Program.

*CLP-M modified for the Contract Laboratory Program.

CALCIUM

Method 215.1 CLP-M* (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.2-7 mg/L using a wavelength of 422.7 nm

Sensitivity: 0.08 mg/L

Detection Limit: 0.01 mg/L

Preparation of Standard Solution

1. Stock Solution: Suspend 1.250 g of CaCO_3 (analytical reagent grade), dried at 180°C for 1 hour before weighing, in deionized distilled water and dissolve cautiously with a minimum of dilute HCl. Dilute to 1000 mL with deionized distilled water. 1 mL = 0.5 mg Ca (500 mg/L).
2. Lanthanum chloride solution: Dissolve 29 g of La_2O_3 , slowly and in small portions, in 250 mL conc. HCl (Caution: Reaction is violent) and dilute to 500 mL with deionized distilled water.
3. Prepare dilutions of the stock calcium solutions to be used as calibration standards at the time of analysis. To each 10 mL of calibration standard and sample alike add 1.0 mL of the lanthanum chloride solution, i.e., 20 mL of standard or sample + 2 mL LaCl_3 = 22 mL.

Instrumental Parameters (General)

1. Calcium hollow cathode lamp
2. Wavelength: 422.7 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Reducing

Notes

1. Phosphate, sulfate and aluminum interfere but are masked by the addition of lanthanum. Because low calcium values result if the pH of the sample is above 7, both standards and samples are prepared in dilute hydrochloric acid solution. Concentrations of magnesium greater than 1000 mg/L also cause low calcium values. Concentrations of up to 500 mg/L each of sodium, potassium and nitrate cause no interference.
2. Anionic chemical interferences can be expected if lanthanum is not used in samples and standards.
3. The nitrous oxide-acetylene flame will provide two to five times greater sensitivity and freedom from chemical interferences. Ionization interferences should be controlled by adding a large amount of alkali to the sample and standards. The analysis appears to be free from chemical suppressions in the nitrous oxide-acetylene flame. (Atomic Absorption Newsletter 14, 29 [1975]).
4. The 239.9 nm line may also be used. This line has a relative sensitivity of 120.

*CLP-M modified for the Contract Laboratory Program.

MAGNESIUM

Method 242.1 CLP-M* (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.02-0.5 mg/L using a wavelength of 285.2 nm

Sensitivity: 0.007 mg/L

Detection Limit: 0.001 mg/L

Preparation of Standard Solution

1. Stock Solution: Dissolve 0.829 g of magnesium oxide, MgO (analytical reagent grade), in 10 mL of redistilled HNO₃ and dilute to 1 liter with deionized distilled water. 1 mL = 0.50 mg Mg (500 mg/L).
2. Lanthanum chloride solution: Dissolve 29 g of La₂O₃, slowly and in small portions in 250 mL concentrated HCl (Caution: Reaction is violent), and dilute to 500 mL with deionized distilled water.
3. Prepare dilutions of the stock magnesium solution to be used as calibration standards at the time of analysis. To each 10 mL volume of calibration standard and sample alike add 1.0 mL of the lanthanum chloride solution, i.e., 20 mL of standard or sample + 2 mL LaCl₃ = 22 mL.

Instrumental Parameters (General)

1. Magnesium hollow cathode lamp
2. Wavelength: 285.2 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. The interference caused by aluminum at concentrations greater than 2 mg/L is masked by addition of lanthanum. Sodium, potassium and calcium cause no interference at concentrations less than 400 mg/L.
2. The following line may also be used: 202.5 nm Relative Sensitivity 25.
3. To cover the range of magnesium values normally observed in surface waters (0.1-20 mg/L), it is suggested that either the 202.5 nm line be used or the burner head be rotated. A 90° rotation of the burner head will produce approximately one-eighth the normal sensitivity.

*CLP-M modified for the Contract Laboratory Program.

POTASSIUM

Method 258.1 CLP-M* (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.1-2 mg/L using a wavelength of 766.5 nm

Sensitivity: 0.04 mg/L

Detection Limit: 0.01 mg/L

Preparation of Standard Solution

1. Stock Solution: Dissolve 0.1907 g of KCl (analytical reagent grade), dried at 110°C, in deionized distilled water and make up to 1 liter. 1 mL = 0.10 mg K (100 mg/L).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Instrumental Parameters (General)

1. Potassium hollow cathode lamp
2. Wavelength: 766.5 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Slightly oxidizing

Notes

1. In air-acetylene or other high temperature flames (>2800°C), potassium can experience partial ionization which indirectly affects absorption sensitivity. The presence of other alkali salts in the sample can reduce this ionization and thereby enhance analytical results. The ionization suppressive effect of sodium is small if the ratio of Na to K is under 10. Any enhancement due to sodium can be stabilized by adding excess sodium (1000 ug/mL) to both sample and standard solutions. If more stringent control of ionization is required, the addition of cesium should be considered. Reagent blanks must be analyzed to correct for potassium impurities in the buffer zone.
2. The 404.4 nm line may also be used. This line has a relative sensitivity of 500.
3. To cover the range of potassium values normally observed in surface waters (0.1-20 mg/L), it is suggested that the burner head be rotated. A 90° rotation of the burner head provides approximately one-eighth the normal sensitivity.

*CLP-M modified for the Contract Laboratory Program.

SODIUM

Method 273.1 CLP-M* (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.03-1 mg/L using a wavelength of 589.6 nm

Sensitivity: 0.015 mg/L

Detection Limit: 0.002 mg/L

Preparation of Standard Solutions

1. Stock Solution: Dissolve 2.542 g of NaCl (analytical reagent grade), dried at 140°C, in deionized distilled water and make up to 1 liter. 1 mL = 1 mg Na (1000 mg/L).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Instrumental Parameters (General)

1. Sodium hollow cathode lamp
2. Wavelength: 589.6 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. The 330.2 nm resonance line of sodium, which has a relative sensitivity of 185, provides a convenient way to avoid the need to dilute more concentrated solutions of sodium.
2. Low-temperature flames increase sensitivity by reducing the extent of ionization of this easily ionized metal. Ionization may also be controlled by adding potassium (1000 mg/L) to both standards and samples.

*CLP-M modified for the Contract Laboratory Program.

PART D - COLD VAPOR METHODS FOR MERCURY ANALYSIS⁺

<u>Method</u>	<u>Page No.</u>
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⁺A bibliography citing method references follows each method.

*CLP-M modified for the Contract Laboratory Program.

MERCURY ANALYSIS IN WATER BY MANUAL COLD VAPOR TECHNIQUE

MERCURY

Method 245.1 CLP-M* (Manual Cold Vapor Technique)

1. Scope and Application

- 1.1 In addition to inorganic forms of mercury, organic mercurials may also be present. These organo-mercury compounds will not respond to the cold vapor atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds, but recent studies have shown that a number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, a persulfate oxidation step following the addition of the permanganate has been included to insure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement. A heat step is required for methyl mercuric chloride when present in or spiked to a natural system. For distilled water the heat step is not necessary.
- 1.2 The range of the method may be varied through instrument and/or recorder expansion. Using a 100 mL sample, a detection limit of 0.2 ug Hg/L can be achieved (See 10.2).

2. Summary of Method

- 2.1 The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. Organic mercury compounds are oxidized and the mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration and recorded in the usual manner.

3. Sample Handling and Preservation

- 3.1 Until more conclusive data are obtained, samples are preserved by acidification with nitric acid to a pH of 2 or lower immediately at the time of collection (Exhibit D, Section II).

*CLP-M modified for the Contract Laboratory Program.

4. Interference

- 4.1 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 mg/l of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from distilled water (Exhibit D, Section II).
- 4.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.
- 4.3 Sea waters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 mL). During the oxidation step, chlorides are converted to free chlorine which will also absorb radiation of 253 nm. Care must be taken to assure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). Both inorganic and organic mercury spikes have been quantitatively recovered from the sea water using this technique.
- 4.4 While the possibility of absorption from certain organic substances actually being present in the sample does exist, EMSL has not encountered such samples. This is mentioned only to caution the analyst of the possibility.

5. Apparatus

- 5.1 Atomic Absorption Spectrophotometer: (See Note 1) Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

NOTE 1: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

- 5.2 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.
- 5.3 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.
- 5.4 Absorption Cell: Standard spectrophotometer cells 10 cm long, having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing, 1" O.D. X 4-1/2". The ends are ground perpendicular to the longitudinal axis and quartz windows (1" diameter X 1/16" thickness) are cemented in place.

The cell is strapped to a burner for support and aligned in the light beam by use of two 2" by 2" cards. One inch diameter holes are cut in the middle of each card; the cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to find the maximum transmittance.

- 5.5 Air Pump: Any peristaltic pump capable of delivering 1 liter of air per minute may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.
- 5.6 Flowmeter: Capable of measuring an air flow of 1 liter per minute.
- 5.7 Aeration Tubing: A straight glass fit having a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.
- 5.8 Drying Tube: 6" X 3/4" diameter tube containing 20 g of magnesium perchlorate (see Note 2). The apparatus is assembled as shown in Figure 1.

NOTE 2: In place of the magnesium perchlorate drying tube, a small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

6. Reagents

- 6.1 Sulfuric Acid, Conc: Reagent grade.
 - 6.1.1 Sulfuric acid, 0.5 N: Dilute 14.0 mL of conc. sulfuric acid to 1.0 liter.
- 6.2 Nitric Acid, Conc: Reagent grade of low mercury content (see Note 3).
 - NOTE 3: If a high reagent blank is obtained, it may be necessary to distill the nitric acid.
- 6.3 Stannous Sulfate: Add 25 g stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)
- 6.4 Sodium Chloride-Hydroxylamine Sulfate Solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in distilled water and dilute to 100 mL. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)
- 6.5 Potassium Permanganate: 5% solution, w/v. Dissolve 5 g of potassium permanganate in 100 mL of distilled water.

- 6.6 Potassium Persulfate: 5% solution, w/v. Dissolve 5 g of potassium persulfate in 100 mL of distilled water.
- 6.7 Stock Mercury Solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of distilled water. Add 10 mL of conc. nitric acid and adjust the volume to 100.0 mL. 1 mL = 1 mg Hg.

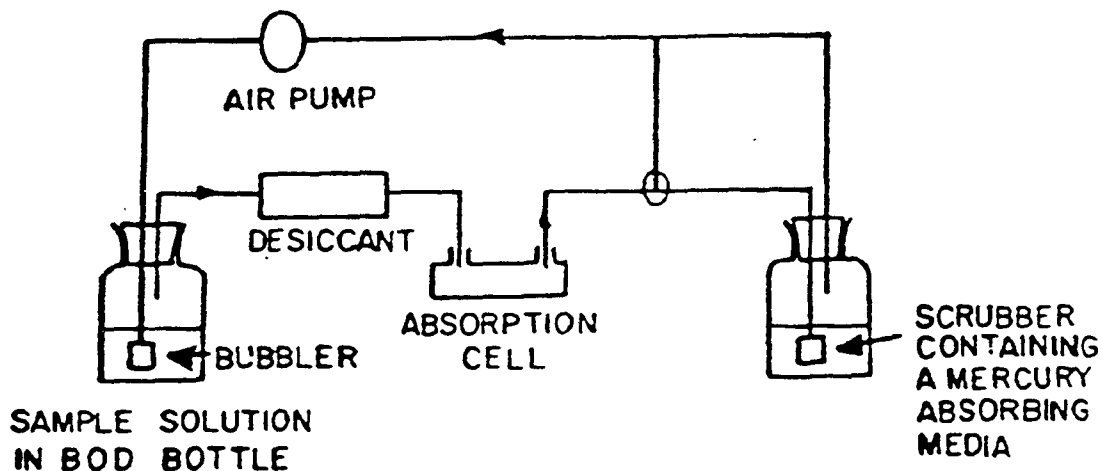


Figure 1. Apparatus for Flameless Mercury Determination

- 6.8 Working Mercury Solution: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 ug per mL. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

7. Calibration

- 7.1 Transfer 0, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working mercury solution containing 0 to 1.0 ug of mercury to a series of 300 mL BOD bottles. Add enough distilled water to each bottle to make a total volume of 100 mL. Mix thoroughly and add 5 mL of conc. sulfuric acid (6.1) and 2.5 mL of conc. nitric acid (6.2) to each bottle. Add 15 mL of KMnO_4 (6.5) solution to each bottle and allow to stand at least 15 minutes. Add 8 mL of potassium persulfate (6.6) to each bottle and heat for 2 hours in a water bath maintained at 95°C. Alternatively, cover the BOD bottles with foil and heat in an autoclave for 15 minutes at 120°C and 15 lbs. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. When the solution has been decolorized wait 30 seconds, add 5 mL of the stannous sulfate solution (6.3) and immediately attach the bottle to the aeration apparatus forming a closed system. At this point the sample is allowed to stand quietly without manual agitation.

The circulating pump, which has previously been adjusted to a rate of 1 liter per minute, is allowed to run continuously (see Note 4). The absorbance will increase and reach maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass valve and continue the aeration until the absorbance returns to its minimum value (see Note 5). Close the bypass valve, remove the stopper and frit from the BOD bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting peak height versus micrograms of mercury.

NOTE 4: An open system where the mercury vapor is passed through the absorption cell only once may be used instead of the closed system.

NOTE 5: Because of the toxic nature of mercury vapor precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as:

- a) equal volumes of 0.1 M KMnO_4 , and 10% H_2SO_4 or
- b) 0.25% iodine in a 3% KI solution. A specially treated charcoal that will adsorb mercury vapor is available.

8. Procedure

- 8.1 Transfer 100 mL, or an aliquot diluted to 100 mL, containing not more than 1.0 ug of mercury, to a 300 mL BOD bottle. Add 5 mL of sulfuric acid (6.1) and 2.5 mL of conc. nitric acid (6.2) mixing after each addition. Add 15 mL of potassium permanganate solution (6.5) to each sample bottle (see Note 6). For sewage samples additional permanganate may be required. Shake and add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 minutes. Add 8 mL of potassium persulfate (6.6) to each bottle and heat for 2 hours in a water bath at 95°C.

NOTE 6: The same amount of KMnO_4 added to the samples should be present in standards and blanks.

Cool and add 6 mL of sodium chloride-hydroxylamine sulfate (6.4) to reduce the excess permanganate (see Note 7). Purge the head space in the BOD bottle for at least 1 minute and add 5 mL of Stannous Sulfate (6.3) and immediately attach the bottle to the aeration apparatus. Continue as described under Calibration.

NOTE 7: Add reductant in 6 mL increments until KMnO_4 is completely reduced.

9. Calculation

- 9.1 Determine the peak height of the unknown from the chart and read the mercury value from the standard curve.
- 9.2 Calculate the mercury concentration in the sample by the formula:

$$\text{ug Hg/L} = \frac{\text{ug Hg in aliquot} \times 1,000}{\text{volume of aliquot in mL}}$$

- 9.3 Report mercury concentrations as follows: Below 0.20 ug/L, 0.20 u; between 0.20 and 10.0 ug/L, two significant figures; equal to or above 10.0 ug/L, three significant figures.

10. Appendix

- 10.1 If additional sensitivity is required, a 200 mL sample with recorder expansion may be used provided the instrument does not produce undue noise. Using a Coleman MAS-50 with a drying tube of magnesium perchlorate and a variable recorder, 2 mv was set to read full scale. With these conditions, and distilled water solutions of mercuric chloride at concentrations of 0.15, 0.10, 0.05 and 0.025 ug/L the standard deviations were ± 0.027 , ± 0.0006 , ± 0.01 and ± 0.004 . Percent recoveries at these levels were 107, 83, 84 and 96%, respectively.
- 10.2 Directions for the disposal of mercury-containing wastes are given in ASTM Standards, Part 31, "Water", p. 349, Method D3223 (1976).

Bibliography

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3. Standard Methods for the Examination of Water and Wastewater 14th Edition, p. 156 (1975).

MERCURY ANALYSIS IN WATER BY AUTOMATED COLD VAPOR TECHNIQUE

MERCURY

Method 245.2 CLP-M* (Automated Cold Vapor Technique)

1. Scope and Application

- 1.1 The working range is 0.2 to 20.0 ug Hg/L.

2. Summary of Method

- 2.1 The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration and recorded in the usual manner.
- 2.2 In addition to inorganic forms of mercury, organic mercurials may also be present. These organo-mercury compounds will not respond to the flameless atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds, but recent studies have shown that a number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, an automated persulfate oxidation step following the automated addition of the permanganate has been included to insure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement.

3. Sample Handling and Preservation

- 3.1 Until more conclusive data are obtained, samples are preserved by acidification with nitric acid to a pH of 2 or lower immediately at the time of collection (Exhibit D, Section II).

4. Interferences (see NOTE 1)

- 4.1 Some sea waters and waste-waters high in chlorides have shown a positive interference, probably due to the formation of free chlorine.

*CLP-M modified for the Contract Laboratory Program.

- 4.2 Formation of a heavy precipitate, in some wastewaters and effluents, has been reported upon addition of concentrated sulfuric acid. If this is encountered, the problem sample cannot be analyzed by this method.
- 4.3 Samples containing solids must be blended and then mixed while being sampled if total mercury values are to be reported.

NOTE 1: All of the above interferences can be overcome by use of the Manual Mercury method.

5. Apparatus

5.1 Technicon Auto Analyzer or equivalent instrumentation consisting of:

- 5.1.1 Sampler II with provision for sample mixing.
- 5.1.2 Manifold.
- 5.1.3 Proportioning Pump II or III.
- 5.1.4 High temperature heating bath with two distillation coils (Technicon Part #116-0163) in series.

5.2 Vapor-liquid separator (Figure 1).

5.3 Absorption cell, 100 mm long, 10 mm diameter with quartz windows.

5.4 Atomic Absorption Spectrophotometer (see Note 2): Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

NOTE 2: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

5.5 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.

5.6 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

6. Reagents
- 6.1 Sulfuric Acid, Conc: Reagent grade
- 6.1.1 Sulfuric acid, 2 N: Dilute 56 mL of conc. sulfuric acid to 1 liter with distilled water.
- 6.1.2 Sulfuric acid, 10%: Dilute 100 mL conc. sulfuric acid to 1 liter with distilled water.
- 6.2 Nitric acid, Conc: Reagent grade of low mercury content.
- 6.2.1. Nitric Acid, 0.5% Wash Solution: Dilute 5 mL of concentrated nitric acid to 1 liter with distilled water.
- 6.3 Stannous Sulfate (See Note 3): Add 50 g stannous sulfate to 500 mL of 2 N sulfuric acid (6.1.1). This mixture is a suspension and should be stirred continuously during use.
- NOTE 3: Stannous chloride may be used in place of stannous sulfate.
- 6.4 Sodium Chloride-Hydroxylamine Sulfate (See Note 4) Solution: Dissolve 30 g of sodium chloride and 30 g of hydroxylamine sulfate in distilled water to 1 liter.
- NOTE 4: Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.
- 6.5 Potassium Permanganate: 0.5% solution, w/v. Dissolve 5 g of potassium permanganate in 1 liter of distilled water.
- 6.6 Potassium Permanganate, 0.1 N: Dissolve 3.16 g of potassium permanganate in distilled water and dilute to 1 liter.
- 6.7 Potassium Persulfate: 0.5% solution, w/v. Dissolve 5 g potassium persulfate in 1 liter of distilled water.
- 6.8 Stock Mercury Solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of distilled water. Add 10 mL of conc. nitric acid and adjust the volume to 100.0 mL. 1.0 mL = 1.0 mg Hg.
- 6.9 Working Mercury Solution: Make successive dilutions of the stock mercury solution (6.8) to obtain a working standard containing 0.1 ug per mL. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot. From this solution prepare standards containing 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, 15.0 and 20.0 ug Hg/L.
- 6.10 Air Scrubber Solution: Mix equal volumes of 0.1 N potassium permanganate (6.6) and 10% sulfuric acid (6.1.2).

7. Procedure (See Note 5)
- 7.1 Set up manifold as shown in Figure 2.
- 7.2 Feeding all the reagents through the system with acid wash solution (6.2.1) through the sample line, adjust heating bath to 105°C.
- 7.3 Turn on atomic absorption spectrophotometer, adjust instrument settings as recommended by the manufacturer, align absorption cell in light path for maximum transmittance and place heat lamp directly over absorption cell.
- 7.4 Arrange working mercury standards from 0.2 to 20.0 ug Hg/L in sampler and start sampling. Complete loading of sample tray with unknown samples.
- 7.5 Prepare standard curve by plotting peak height of processed standards against concentration values. Determine concentration of samples by comparing sample peak height with standard curve.
- 7.6 After the analysis is complete put all lines except the H₂SO₄ line in distilled water to wash out system. After flushing, wash out the H₂SO₄ line. Also flush the coils in the high temperature heating bath by pumping stannous sulfate (6.3) through the sample lines followed by distilled water. This will prevent build-up of oxides of manganese.

NOTE 5: Because of the toxic nature of mercury vapor, precaution must be taken to avoid its inhalation. Venting the mercury vapor into an exhaust hood or passing the vapor through some absorbing media such as: a) equal volumes of 0.1 N KMnO₄ (6.6) and 10% H₂SO₄ (6.1.2), or b) 0.25% iodine in a 3% KI solution, is recommended. A specially treated charcoal that will absorb mercury vapor is also available.

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7. Op. cit. (#1), Methods 245.1 or 245.2.

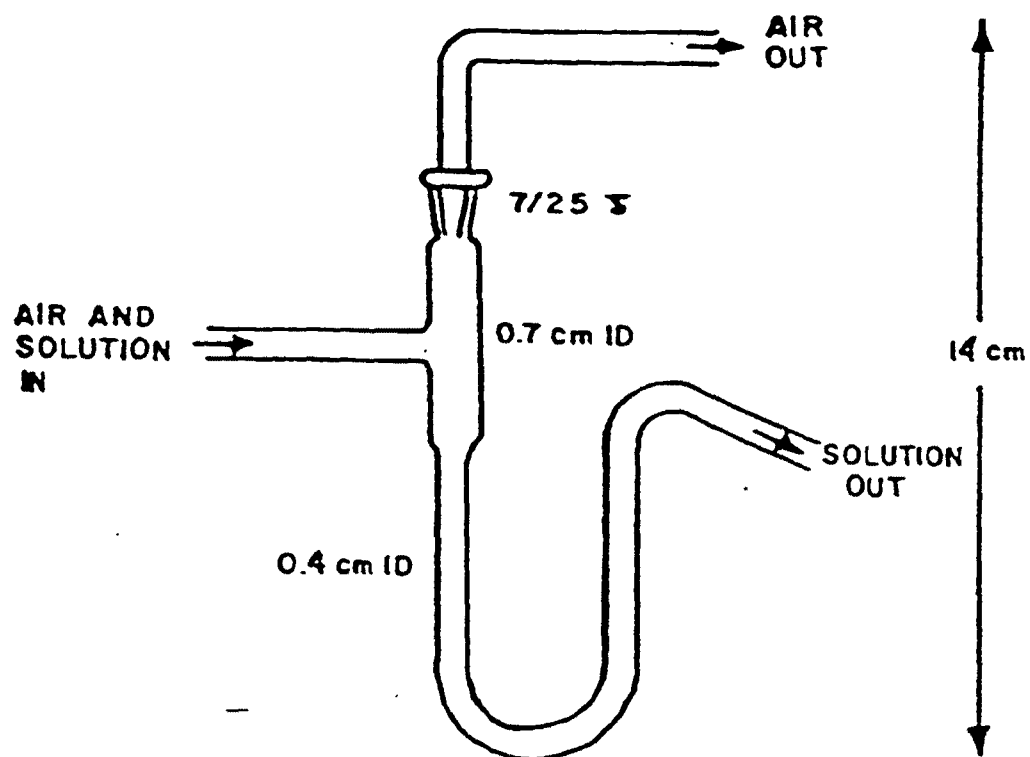


Figure 1. Vapor liquid separator
D-54

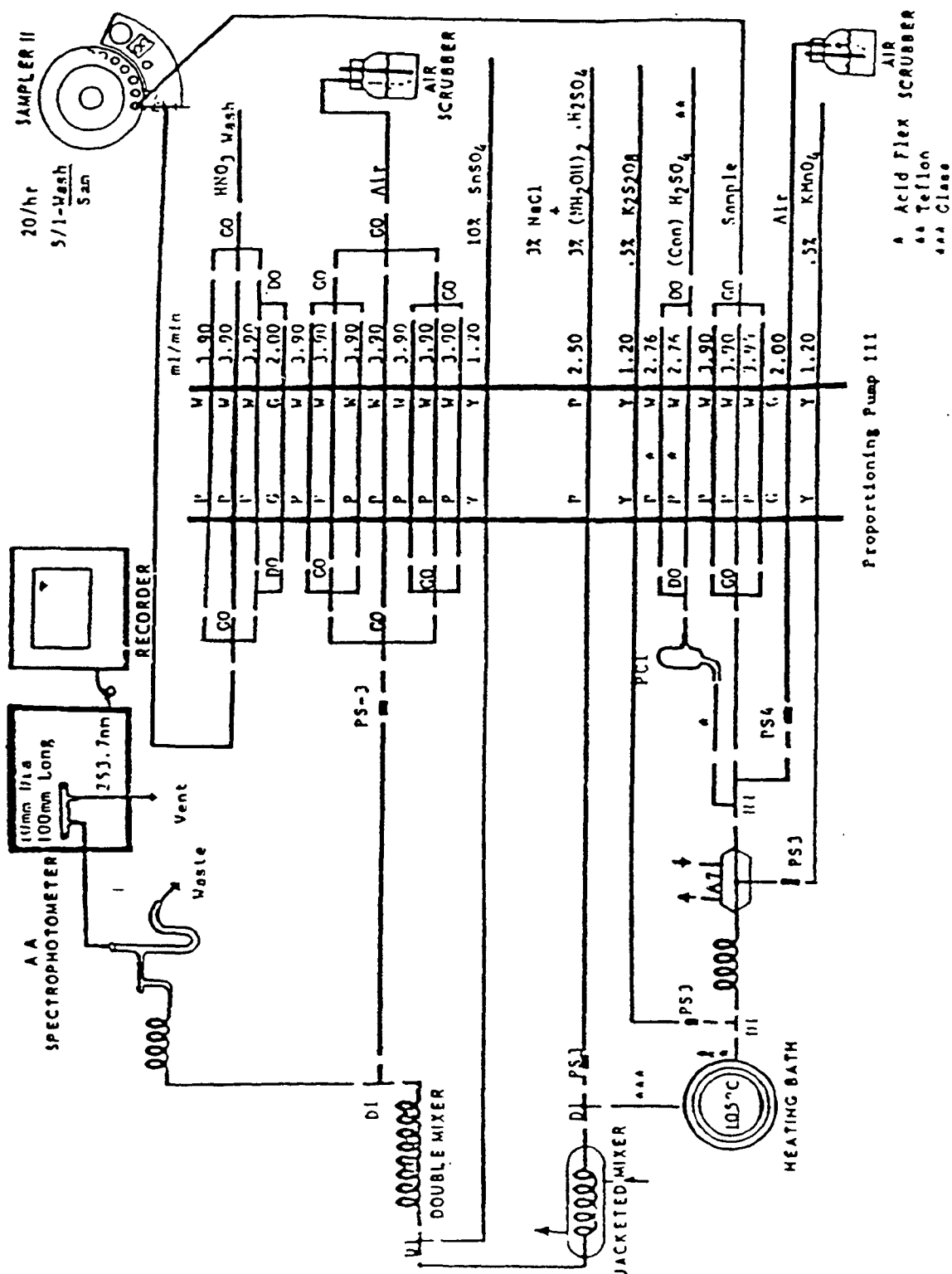


Figure 2. Mercury Manifold AA-1
D-55

MERCURY ANALYSIS IN SOIL/SEDIMENT BY MANUAL COLD VAPOR TECHNIQUE

MERCURY (in Sediments) Method 245.5 CLP-M* (Manual Cold Vapor Technique)

1. Scope and Application

- 1.1 This procedure measures total mercury (organic and inorganic) in soils, sediments, bottom deposits and sludge type materials
- 1.2 The range of the method is 0.2 to 5 ug/g. The range may be extended above or below the normal range by increasing or decreasing sample size or through instrument and recorder control

2. Summary of Method

- 2.1 A weighed portion of the sample is acid digested for 2 minutes at 95°C, followed by oxidation with potassium permanganate and potassium persulfate. Mercury in the digested sample is then measured by the conventional cold vapor technique
- 2.2 An alternate digestion involving the use of an autoclave is described in (8.2)

3. Sample Handling and Preservation

- 3.1 Because of the extreme sensitivity of the analytical procedure and the omnipresence of mercury, care must be taken to avoid extraneous contamination. Sampling devices and sample containers should be ascertained to be free of mercury; the sample should not be exposed to any condition in the laboratory that may result in contact or air-borne mercury contamination
- 3.2 Refrigerate solid samples at 4°C ($\pm 2^\circ$) upon receipt until analysis (see Exhibit D, Section II).
- 3.3 The sample should be analyzed without drying. A separate percent solids determination is required, (Part F).

4. Interferences

- 4.1 The same types of interferences that may occur in water samples are also possible with sediments, i.e., sulfides, high copper, high chlorides, etc.
- 4.2 Samples containing high concentrations of oxidizable organic materials, as evidenced by high chemical oxygen demand values, may not be completely oxidized by this procedure. When this

*CLP-M modified for the Contract Laboratory Program.

occurs, the recovery of organic mercury will be low. The problem can be eliminated by reducing the weight of the original sample or by increasing the amount of potassium persulfate (and consequently stannous chloride) used in the digestion.

5. Apparatus

- 5.1 Atomic Absorption Spectrophotometer (see Note 1): Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed

NOTE 1: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer

- 5.2 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent
- 5.3 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.
- 5.4 Absorption Cell: Standard spectrophotometer cells 10 cm long, having quartz end windows may be used. Suitable cells may be constructed from pexiglass tubing, 1" O.D. X 4-1/2". The ends are ground perpendicular to the longitudinal axis and quartz windows (1" diameter X 1/16" thickness) are cemented in place. Gas inlet and outlet ports (also of plexiglass but 1/4" O.D.) are attached approximately 1/2" from each end. The cell is strapped to a burner for support and aligned in the light beam to give the maximum transmittance. Two 2" X 2" cards with one inch diameter holes may be placed over each end of the cell to assist in positioning the cell for maximum transmittance.
- 5.5 Air Pump: Any peristaltic pump capable of delivering 1 liter of air per minute may be used. A Masterflex pump with electronic speed control has been found to be satisfactory. (Regulated compressed air can be used in an open one-pass system.)
- 5.6 Flowmeter: Capable of measuring an air flow of 1 liter per minute
- 5.7 Aeration Tubing: Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return. Straight glass tubing terminating in a coarse porous frit is used for sparging air into the sample
- 5.8 Drying Tube: 6" X 3/4" diameter tube containing 20 g of magnesium perchlorate (see Note 2).

NOTE 2: In place of the magnesium perchlorate drying tube, a small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

6. Reagents

- 6.1 Sulfuric acid, conc.: Reagent grade of low mercury content
- 6.2 Nitric acid, conc.: Reagent grade of low mercury content
- 6.3 Stannous Sulfate: Add 25 g stannous sulfate to 250 mL of 0.5 N sulfuric acid (6.2). This mixture is a suspension and should be stirred continuously during use
- 6.4 Sodium Chloride-Hydroxylamine Sulfate (See Note 3) Solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in distilled water and dilute to 100 mL

NOTE 3: A 10% solution of stannous chloride may be substituted for (6.3) and hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate in (6.4)

- 6.5 Potassium Permanganate: 5% solution, w/v. Dissolve 5 g of potassium permanganate in 100 mL of distilled water
- 6.6 Potassium Persulfate: 5% solution, w/v. Dissolve 5 g of potassium persulfate in 100 mL of distilled water
- 6.7 Stock Mercury Solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of distilled water. Add mL of conc. nitric acid and adjust the volume to 100.0 mL. 1.0 = 1.0 mg Hg
- 6.8 Working Mercury Solution: Make successive dilutions of the stock mercury solution (6.7) to obtain a working standard containing 0.1 ug/mL. This working standard and the dilution of the stock mercury solutions should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot

7. Calibration

- 7.1 Transfer 0, 0.5, 1.0, 5.0 and 10 mL aliquots of the working mercury solutions (6.8) containing 0 to 1.0 ug of mercury to a series of 300 mL BOD bottles. Add enough distilled water to each bottle to make a total volume of 10 mL. Add 5 mL of conc. H_2SO_4 (6.1) and 2.5 mL of conc. HNO_3 (6.2) and heat 2 minutes in a water bath at 95°C. Allow the sample to cool and add 50 mL distilled water, 15 mL of $KMnO_4$ solution (6.5) and 8 mL of potassium persulfate solution (6.6) to each bottle and return to the water bath for 30 minutes. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. Add 50 mL of distilled water. Treating each bottle individually, add 5 mL of stannous sulfate

solution (6.3) and immediately attach the bottle to the aeration apparatus. At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter per minute, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass valve and continue the aeration until the absorbance returns to its minimum value (see Note 4). Close the bypass valve, remove the fritted tubing from the BOD bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting peak height versus micrograms of mercury

NOTE 4: Because of the toxic nature of mercury vapor, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as: a) equal volumes of 0.1 N KMnO_4 and 10% H_2SO_4 , or b) 0.25% iodine in a 3% KI solution. A specially treated charcoal that will absorb mercury vapor is also available.

8. Procedure

- 8.1 Weigh a representative 0.2 g portion of wet sample and place in the bottom of a BOD bottle. Add 5 mL of sulfuric acid (6.1) and 2.5 mL of concentrated nitric acid (6.2) mixing after each addition. Heat two minutes in a water bath at 95°C. Cool, add 50 mL distilled water, 15 mL potassium permanganate solution (6.5) and 8 mL of potassium persulfate solution (6.6) to each sample bottle. Mix thoroughly and place in the water bath for 30 minutes at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate (6.4) to reduce the excess permanganate. Add 55 mL of distilled water. Treating each bottle individually, purge the head space of the sample bottle for at least one minute and add 5 mL of stannous sulfate (6.3) and immediately attach the bottle to the aeration apparatus. Continue as described under (7.1)
- 8.2 An alternate digestion procedure employing an autoclave may also be used. In this method 5 mL of conc. H_2SO_4 and 2 mL of conc. HNO_3 are added to the 0.2 g of sample. 5 mL of saturated KMnO_4 solution and 8 mL of potassium persulfate solution are added and the bottle is covered with a piece of aluminum foil. The sample is autoclaved at 121°C and 15 lbs. for 15 minutes. Cool, make up to a volume of 100 mL with distilled water and add 6 mL of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. Purge the head space of the sample bottle for at least one minute and continue as described under (7.1)

9. Calculations

- 9.1 Measure the peak height of the unknown from the chart and read the mercury value from the standard curve
- 9.2 Calculate the mercury concentration in the sample by the formula:

$$\text{ug Hg/g} = \frac{\text{ug Hg in the aliquot}}{\text{wt of the aliquot in gms}} \\ \text{(based upon dry wt of the sample)}$$

- 9.3 Report mercury concentrations as described for aqueous mercury samples converted to units of mg/kg. The sample result or the detection limit for each sample must be corrected for sample weight and % solids before reporting.

Note that the minimum reportable number that can be substituted in the formula in section 9.2 is 0.02 ug Hg in the aliquot. Therefore a sample with a weight of 0.2 grams and 100 % solids that has a reading from the curve of less than 0.02 ug would be reported as 0.10U mg/kg.

Bibliography

1. Bishop, J. N., "Mercury in Sediments", Ontario Water Resources Comm., Toronto, Ontario, Canada, 1971
2. Salma, M., private communication, EPA Cal/Nev. Basin Office, Alameda, California
3. "Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue," USEPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, August 1977, Revised October 1980
4. Op. cit. (#3), Methods 245.1 or 245.2

PART E - METHODS FOR CYANIDE ANALYSIS⁺

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⁺A bibliography citing method references follows each method.

*CLP-M Modified for the Contract Laboratory Program.

METHOD FOR TOTAL CYANIDE ANALYSIS IN WATER

CYANIDE, TOTAL (in Water)

Method 335.2 CLP-M* (Titrimetric; Manual Spectrophotometric; Semi-Automated Spectrophotometric)

1. Scope and Application

- 1.1 This method is applicable to the determination of cyanide in drinking, surface and saline waters, domestic and industrial wastes.
- 1.2 The titration procedure using silver nitrate with p-dimethylaminobenzalrhodanine indicator is used for measuring concentrations of cyanide exceeding 1 mg/L (0.25 mg/250 mL of absorbing liquid). (Option A, 8.2).
- 1.3 The manual colorimetric procedure is used for concentrations below 1 mg/L of cyanide and is sensitive to about 0.02 mg/L. (Option B, 8.3).
- 1.4 The working range of the semi-automated spectrophotometric method is 0.005 to 0.200 mg/L. Higher level samples must be diluted to fall within the working range. (Option C, 8.4).

2. Summary of Method

- 2.1 The cyanide as (HRN) hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by volumetric titration or colorimetrically.
- 2.2 In the colorimetric measurement the cyanide is converted to cyanogen chloride, $CNCl$, by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-pyrazolone or pyridinebarbituric acid reagent. The absorbance is read at 620 nm when using pyridine-pyrazolone or 578 nm for pyridine-barbituric acid. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.
- 2.3 The titimetric measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver sensitive indicator.

3. Definitions

- 3.1 Cyanide is defined as cyanide ion and complex cyanides converted to hydrocyanic acid (HCN) by reaction in a reflux system of a mineral acid in the presence of magnesium ion.

*CLP-M Modified for the Contract Laboratory Program.

4. Sample Handling and Preservation

- 4.1 All bottles must be thoroughly cleansed and rinsed to remove soluble material from containers.
- 4.2 Oxidizing agents such as chlorine decompose most of the cyanides. Test a drop of the sample with potassium iodide-starch test paper (KI-starch paper); a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper. Then add an additional 0.6 g of ascorbic acid for each liter of sample volume.
- 4.3 Samples are preserved with 2 mL of 10 N sodium hydroxide per liter of sample (pH > 12) at the time of collection (Exhibit D, Section II).
- 4.4 Samples must be stored at 4°C (±2°C) and must be analyzed within the holding time specified in Exhibit D, Section II.

5. Interferences

- 5.1 Interferences are eliminated or reduced by using the distillation procedure described in Procedure 8.1.
- 5.2 Sulfides adversely affect the colorimetric and titration procedures. If a drop of the distillate on lead acetate test paper indicates the presence of sulfides, treat 25 mL more of the sample than that required for the cyanide determination with powdered cadmium carbonate. Yellow cadmium sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution through a dry filter paper into a dry beaker, and from the filtrate measure the sample to be used for analysis. Avoid a large excess of cadmium carbonate and a long contact time in order to minimize a loss by complexation or occlusion of cyanide on the precipitated material. Sulfides should be removed prior to preservation with sodium hydroxide as described in 4.3.
- 5.3 The presence of surfactants may cause the sample to foam during refluxing. If this occurs, the addition of an agent such as Dow Corning 544 antifoam agent will prevent the foam from collecting in the condenser. Fatty acids will distill and form soaps under alkaline titration conditions, making the end point almost impossible to detect. When this occurs, one of the spectrophotometric methods should be used.

6. Apparatus

- 6.1 Reflux distillation apparatus such as shown in Figure 1 or Figure 2. The boiling flask should be of 1 liter size with inlet tube and provision for condenser. The gas absorber may be a Fisher-Milligan scrubber.
- 6.2 Microburet, 5.0 mL (for titration)

- 6.3 Spectrophotometer suitable for measurements at 578 nm or 620 nm with a 1.0 cm cell or larger (for manual spectrophotometric method).
- 6.4 Technicon AA II System or equivalent instrumentation, (for automated spectrophotometric method) including:
 - 6.4.1 Sampler
 - 6.4.2 Pump III
 - 6.4.3 Cyanide Manifold (Figure 3)
 - 6.4.4 SCIC Colorimeter with 15 mm flowcells and 570 nm filters
 - 6.4.5 Recorder
 - 6.4.6 Data System (optional)
 - 6.4.7 Glass or plastic tubes for the sampler

7. Reagents

7.1 Distillation and Preparation Reagents

- 7.1.1 Sodium hydroxide solution, 1.25N: Dissolve 50 g of NaOH in distilled water, and dilute to 1 liter with distilled water.
- 7.1.2 Cadmium carbonate: powdered
- 7.1.3 Ascorbic acid: crystals
- 7.1.4 Sulfuric acid: concentrated
- 7.1.5 Magnesium chloride solution: Weigh 510 g of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ into a 1000 mL flask, dissolved and dilute to 1 liter with distilled water.

7.2 Stock Standards and Titration Reagents

- 7.2.1 Stock cyanide solution: Dissolve 2.51 g of KCN and 2 g KOH in 1 liter of distilled water. Standardize with 0.0192 N AgNO_3 .
- 7.2.2 Standard cyanide solution, intermediate: Dilute 50.0 mL of stock (1 mL = 1 mg CN) to 1000 mL with distilled water.
- 7.2.3 Standard cyanide solution: Prepare fresh daily by diluting 100.0 mL of intermediate cyanide solution to 1000 mL with distilled water and store in a glass stoppered bottle. 1 mL = 5.0 ug CN (5.0 mg/L).

- 7.2.4 Standard silver nitrate solution, 0.0192 N: Prepare by crushing approximately 5 g AgNO_3 crystals and drying to constant weight at 40°C . Weight out 3.2647 g of dried AgNO_3 , dissolve in distilled water, and dilute to 1000 mL (1 mL = 1 mg CN).
- 7.2.5 Rhodanine indicator: Dissolve 20 mg of p-dimethyl-aminobenzalrhodanine in 100 mL of acetone.
- 7.2.6 Sodium hydroxide solution, 0.25 N: Dissolve 10 g of NaOH in distilled water and dilute to 1 liter.

7.3 Manual Spectrophotometric Reagents

- 7.3.1 Sodium dihydrogenphosphate, 1 M: Dissolve 138 g of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ in a liter of distilled water. Refrigerate this solution.
- 7.3.2 Chloramine-T solution: Dissolve 1.0 g of white, water soluble chloramine-T in 100 mL of distilled water and refrigerate until ready to use. Prepare fresh weekly.
- 7.3.3 Color Reagent-One of the following may be used:
 - 7.3.3.1 Pyridine-barbituric acid reagent: Place 15 g of barbituric acid in a 250 mL volumetric flask and add just enough distilled water to wash the sides of the flask and wet the barbituric acid. Add 75 mL of pyridine and mix. Add 15 mL of HCl (sp gr 1.19), mix, and cool to room temperature. Dilute to 250 mL with distilled water and mix. This reagent is stable for approximately six months if stored in a cool, dark place.
 - 7.3.3.2 Pyridine-pyrazolone solution:
 - 7.3.3.2.1 3-Methyl-1-phenyl-2-pyrazolin-5-one reagent, saturated solution: Add 0.25 g of 3-methyl-1-phenyl-2-pyrazolin-5-one to 50 mL of distilled water, heat to 60°C with stirring. Cool to room temperature.
 - 7.3.3.2.2 3,3'-Dimethyl-1,1'-diphenyl [4,4'-bi-2-pyrazolin]-5,5'-dione (bispyrazolone): Dissolve 0.01 g of bispyrazolone in 10 mL of pyridine.

7.3.3.2.3 Pour solution (7.3.3.2.1) through nonacid-washed filter paper. Collect the filtrate. Through the same filter paper pour solution (7.3.3.2.2) collecting the filtrate in the same container as filtrate from (7.3.3.2.1). Mix until the filtrates are homogeneous. The mixed reagent develops a pink color but this does not affect the color production with cyanide if used within 24 hours of preparation.

7.4 Semi-Automated Spectrophotometric Reagents

- 7.4.1 Chloramine-T solution: Dissolve 0.40 g of chloramine-T in distilled water and dilute to 100 mL. Prepare fresh daily.
- 7.4.2 Phosphate buffer: Dissolve 138 g of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ in distilled water and dilute to 1 liter. Add 0.5 mL of Brij-35 (available from Technicon). Store at $4^\circ\text{C}(\pm 2^\circ\text{C})$.
- 7.4.3 Pyridine-barbituric acid solution: Transfer 15 g of barbituric acid into a 1 liter volumetric flask. Add about 100 mL of distilled water and swirl the flask. Add 74 mL of pyridine and mix. Add 15 mL of concentrated HCl and mix. Dilute to about 900 mL with distilled water and mix until the barbituric acid is dissolved. Dilute to 1 liter with distilled water. Store at $4^\circ\text{C}(\pm 2^\circ\text{C})$.
- 7.4.4 Sampler wash: Dissolve 10 g of NaOH in distilled water and dilute to 1 liter.

8. Procedure

8.1 Distillation

- 8.1.1 Place 500 mL of sample, or an aliquot diluted to 500 mL, in the 1 liter boiling flask. Add 50 mL of sodium hydroxide (7.1.1) to the absorbing tube and dilute if necessary with distilled water to obtain an adequate depth of liquid in the absorber. Connect the boiling flask, condenser, absorber and trap in the train.
- 8.1.2 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately one bubble of air per second enters the boiling flask through the air inlet tube.

NOTE: The bubble rate will not remain constant after the reagents have been added and while heat is being applied to the flask. It will be necessary to readjust the air rate occasionally to prevent the solution in the boiling flask from backing up into the air inlet tube.

- 8.1.3 Slowly add 25 mL concentrated sulfuric acid (7.1.4) through the air inlet tube. Rinse the tube with distilled water and allow the airflow to mix the flask contents for 3 minutes. Pour 20 mL of magnesium chloride solution (7.1.5) into the air inlet and wash down with a stream of water.
- 8.1.4 Heat the solution to boiling, taking care to prevent the solution from backing up into and overflowing from the air inlet tube. Reflux for one hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, disconnect absorber and close off the vacuum source.
- 8.1.5 Drain the solution from the absorber into a 250 mL volumetric flask and bring up to volume with distilled water washings from the absorber tube.
- 8.2 Titrimetric Determination (Option A)
- 8.2.1 If the sample contains more than 1 mg of CN, transfer the distillate, or a suitable aliquot diluted to 250 mL, to a 500 mL Erlenmeyer flask. Add 10-12 drops of the benzalrhodanine indicator.
- 8.2.2 Titrate with standard silver nitrate to the first change in color from yellow to brownish-pink. Titrate a distilled water blank using the same amount of sodium hydroxide and indicator as in the sample.
- 8.2.3 The analyst should familiarize himself with the end point of the titration and the amount of indicator to be used before actually titrating the samples. A 5 or 10 mL microburet may be conveniently used to obtain a more precise titration.
- 8.3 Manual Spectrophotometric Determination (Option B)
- 8.3.1 Withdraw 50 mL or less of the solution from the flask and transfer to a 100 mL volumetric flask. If less than 50 mL is taken, dilute to 50 mL with 0.25 N sodium hydroxide solution (7.2.6). Add 15.0 mL of sodium phosphate solution (7.3.1) and mix.
- 8.3.1.1 Pyridine-barbituric acid method: Add 2 mL of chloramine-T (7.3.2) and mix. After 1 to 2 minutes, add 5 mL of pyridine-barbituric acid solution (7.3.3.1) and mix. Dilute to mark with distilled water and mix again. Allow 8 minutes for color development then read absorbance at 578 nm in a 1 cm cell within 15 minutes.

- 8.3.1.2 Pyridine-pyrazolone method: Add 0.5 mL of chloramine-T (7.3.2) and mix. After 1 to 2 minutes, add 5 mL of pyridine-pyrazolone solution (7.3.3.2) and mix. Dilute to mark with distilled water and mix again. After 40 minutes, read absorbance at 620 nm in a 1 cm cell. NOTE: More than 0.5 mL of chloramine-T will prevent the color from developing with pyridine-pyrazolone.
- 8.3.2 Prepare a minimum of 3 standards and a blank by pipetting suitable volumes of standard solution into 250 mL volumetric flasks. NOTE: One calibration standard must be at the Contract Required Detection Limit (CRDL). To each standard, add 50 mL of 1.25 N sodium hydroxide and dilute to 250 mL with distilled water. Standards must bracket the concentration of the samples. If dilution is required, use the blank solution.

As an example, standard solutions could be prepared as follows:

<u>mL of Standard Solution</u> <u>(1.0 = 5 ug CN)</u>	<u>Conc. ug CN</u> <u>per 250 mL</u>
0	Blank
1.0	5
2.0	10
5.0	25
10.0	50
15.0	75
20.0	100

- 8.3.2.1 It is not imperative that all standards be distilled in the same manner as the samples. At least one standard (mid-range) must be distilled and compared to similar values on the curve to ensure that the distillation technique is reliable. If the distilled standard does not agree within $\pm 15\%$ of the undistilled standards, the operator should find and correct the cause of the apparent error before proceeding.
- 8.3.2.2 Prepare a standard curve by plotting absorbance of standard vs. cyanide concentrations (per 250 mL).

8.4 Semi-Automated Spectrophotometric Determination (Option C)

- 8.4.1 Set up the manifold as shown in Figure 3. Pump the reagents through the system until a steady baseline is obtained.
- 8.4.2 Calibration standards: Prepare a blank and at least three calibration standards over the range of the analysis. One calibration standard must be at the CRDL. For a working range of 0-200 ug/L, the following standards may be used:

<u>mL Standard Solution</u> <u>(7.2.3) diluted to 1 liter</u>	<u>Concentration</u> <u>ug CN/L</u>
0	0
4.0	20
10.0	50
20.0	100
30.0	150
40.0	200

Add 10 g of NaOH to each standard. Store at 4°C(±2°C)

8.4.3 Place calibration standards, blanks, and control standards in the sampler tray, followed by distilled samples, distilled duplicates, distilled standards, distilled spikes, and distilled blanks.

8.4.4 When a steady reagent baseline is obtained and before starting the sampler, adjust the baseline using the appropriate knob on the colorimeter. Aspirate a calibration standard and adjust the STD CAL dial on the colorimeter until the desired signal is obtained. Record the STD CAL value. Re-establish the baseline and proceed to analyze calibration standards, blanks, control standards, distilled samples, and distilled QC audits.

9. Calculations

9.1 Using the titrimetric procedure, calculate concentration of CN as follows:

$$\text{CN, mg/L} = \frac{(A-B) 1,000 \text{ mL/L}}{\text{mL orig. sample}} \times \frac{250 \text{ mL}}{\text{mL of aliquot titrated}}$$

WHERE: A = volume of AgNO₃ for titration of sample
(1 mL = 1 mg Ag)

B = volume of AgNO₃ for titration of blank
(1 mL = 1 mg Ag)

AND: 250 mL = distillate volume (See 8.1.5)
1000 mL = conversion mL to L
mL original sample (See 8.1.1)
mL of aliquot titrated (See 8.2.1)

9.2 If the semi-automated method is used, measure the peak heights of the calibration standards (visually or using a data system) and calculate a linear regression equation. Apply the equation to the samples and QC audits to determine the cyanide concentration in the distillates. To determine the concentration of cyanide in the original sample, MULTIPLY THE RESULTS BY ONE-HALF (since the original volume was 500 mL and the distillate volume was 250 mL). Also, correct for any dilutions which were made before or after distillation.

- 9.3 If the colorimetric procedure is used, calculate the cyanide, in ug/L, in the original sample as follows:

$$\text{CN, ug/L} = \frac{A \times 1,000 \text{ mL/L}}{B} \times \frac{50 \text{ mL}}{C}$$

WHERE: A = ug CN read from standard curve (per 250 mL)
B = mL of original sample for distillation (See 8.1.1)
C = mL taken for colorimetric analysis (See 8.3.1)

AND: 50 mL = volume of original sample aliquot (See 8.3.1)
1000 mL/L = conversion mL to L

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1. Methods for "Chemical Analysis of Water and Wastes", March 1979, EPA publication #600/4-79-02.
2. "Operation RN Manual for Technicon Auto Analyzer IIC System", 1980. Technical publication #TA9-0460-00. Technicon Industrial Systems, Tarrytown, NY, 10591.
3. "Users Guide for the Continuous Flow Analyzer Automation System", EMSL U.S. EPA, Cincinnati, OH (1981).
4. Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue," USEPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, August 1977, Revised October 1980.
5. Op. cit. (#4), Methods 335.2.

METHOD FOR TOTAL CYANIDE ANALYSIS IN SOIL/SEDIMENT

CYANIDE, TOTAL (in Sediments)

Method 335.2 CLP-M* (Titrimetric; Manual Spectrophotometric;
Semi-Automated Spectrophotometric)

1. Scope and Application

- 1.1 This method is applicable to the determination of cyanide in sediments and other solids.
- 1.2 The detection limit is dependent upon the weight of sample taken for analysis.

2. Summary of Method

- 2.1 The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by volumetric titration or colorimetrically.
- 2.2 In the colorimetric measurement the cyanide is converted to cyanogen chloride, CNCl, by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-pyrazolone or pyridine-barbituric acid reagent. The absorbance is read at 620 nm when using pyridine-pyrazolone for 578 nm for pyridine-barbituric acid. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.
- 2.3 The titrimetric measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver sensitive indicator.

3. Definitions

- 3.1 Cyanide is defined as cyanide ion and complex cyanides converted to hydrocyanic acid (HCN) by reaction in a reflux system of a mineral acid in the presence of magnesium ion.

4. Sample Handling and Preservation

- 4.1 Samples must be stored at 4°C(+2°C) and must be analyzed within the holding time specified in Exhibit D, Section II.
- 4.2 Samples are not dried prior to analysis. A separate percent solids determination must be made in accordance with the procedure in Part F.

*CLP-M Modified for the Contract Laboratory Program.

5. Interferences

- 5.1 Interferences are eliminated or reduced by using the distillation procedure described in Procedure 8.1.
- 5.2 Sulfides adversely affect the colorimetric and titration procedures.
- 5.3 The presence of surfactants may cause the sample to foam during refluxing. If this occurs, the addition of an agent such as DOW Corning 544 antifoam agent will prevent the foam from collecting in the condenser. Fatty acids will distill and form soaps under the alkaline titration conditions, making the end point almost impossible to detect. When this occurs, one of the spectrophotometric methods should be used.

6. Apparatus

- 6.1 Reflux distillation apparatus such as shown in Figure 1 or Figure 2. The boiling flask should be of 1 liter size with inlet tube and provision for condenser. The gas absorber may be a Fisher-Milligan scrubber.
- 6.2 Microburet, 5.0 mL (for titration)
- 6.3 Spectrophotometer suitable for measurements at 578 nm or 620 nm with a 1.0 cm cell or larger.
- 6.4 Technicon AA II System or equivalent instrumentation (for automated spectrophotometric method) including:
 - 6.4.1 Sampler
 - 6.4.2 Pump III
 - 6.4.3 Cyanide Manifold (Figure 3)
 - 6.4.4 SCIC Colorimeter with 15 mm flowcells and 570 nm filters
 - 6.4.5 Recorder
 - 6.4.6 Data System (optional)
 - 6.4.7 Glass or plastic tubes for the sampler

7. Reagents

- 7.1 Distillation and Preparation Reagents
 - 7.1.1 Sodium hydroxide solution, 1.25N: Dissolve 50 g of NaOH in distilled water, and dilute to 1 liter with distilled water.
 - 7.1.2 Cadmium carbonate: powdered
 - 7.1.3 Ascorbic acid: crystals

- 7.1.4 Sulfuric acid: concentrated
- 7.1.5 Magnesium chloride solution: Weigh 510 g of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ into a 1000 mL flask, dissolve and dilute to 1 liter with distilled water.
- 7.2 Stock Standards and Titration Reagents
 - 7.2.1 Stock cyanide solution: Dissolve 2.51 g of KCN and 2 g KOH in 1 liter of distilled water. Standardize with 0.0192 N AgNO_3 .
 - 7.2.2 Standard cyanide solution, intermediate: Dilute 50.0 mL of stock (1 mL = 1 mg CN) to 1000 mL with distilled water (1 mL = 50.0 ug).
 - 7.2.3 Standard cyanide solution: Prepare fresh daily by diluting 100.0 mL of intermediate cyanide solution to 1000 mL with distilled water and store in a glass stoppered bottle. 1 mL = 5.0 ug CN (5.0 mg/L).
 - 7.2.4 Standard silver nitrate solution, 0.0192 N: Prepare by crushing approximately 5 g AgNO_3 crystals and drying to constant weight at 40°C . Weigh out 3.2647 g of dried AgNO_3 , dissolve in distilled water, and dilute to 1000 mL (1 mL = 1 mg CN).
 - 7.2.5 Rhodanine indicator: Dissolve 20 mg of p-dimethyl-amino-benzalrhodanine in 100 mL acetone.
- 7.3 Manual Spectrophotometric Reagents
 - 7.3.1 Sodium dihydrogenphosphate, 1 M: Dissolve 138 g of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ in 1 liter of distilled water. Refrigerate this solution.
 - 7.3.2 Chloramine-T solution: Dissolve 1.0 g of white, water soluble Chloramine-T in 100 mL of distilled water and refrigerate until ready to use. Prepare fresh weekly.
 - 7.3.3 Color reagent - One of the following may be used:
 - 7.3.3.1 Pyridine-barbituric acid reagent: Place 15 g of barbituric acid in a 250 mL volumetric flask and add just enough distilled water to wash the sides of the flask and wet the barbituric acid. Add 75 mL of pyridine and mix. Add 15 mL of HCl (sp gr 1.19), mix, and cool to room temperature. Dilute to 250 mL with distilled water and mix. This reagent is stable for approximately six months if stored in a cool, dark place.
 - 7.3.3.2 Pyridine-pyrazolone solution:

- 7.3.3.2.1 3-Methyl-1-phenyl-2-pyrazolin-5-one reagent, saturated solution: Add 0.25 g of 3-methyl-1-phenyl-2-pyrazolin-5-one to 50 mL of distilled water, heat to 60°C with stirring. Cool to room temperature.
- 7.3.3.2.2 3,3'-Dimethyl-1,1'-diphenyl-[4,4'-bi-2-pyrazolin]-5,5'-dione (bispyrazolone): Dissolve 0.01 g of bispyrazolone in 10 mL of pyridine.
- 7.3.3.2.3 Pour solution (7.3.3.2.1) through non-acid-washed filter paper. Collect the filtrate. Through the same filter paper pour solution (7.3.3.2.2) collecting the filtrate in the same container as filtrate from (7.3.3.2.1). Mix until the filtrates are homogeneous. The mixed reagent develops a pink color but this does not affect the color production with cyanide if used within 24 hours of preparation.

7.4 Semi-Automated Spectrophotometric Reagents

- 7.4.1 Chloramine-T solution: Dissolve 0.40 g of chloramine-T in distilled water and dilute to 100 mL. Prepare fresh daily..
- 7.4.2 Phosphate Buffer: Dissolve 138 g of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ in distilled water and dilute to 1 liter. Add 0.5 mL of Brij-35 (available from Technicon). Store at 4°C.
- 7.4.3 Pyridine-barbituric acid solution: Transfer 15 g of barbituric acid into a 1 liter volumetric flask. Add about 100 mL of distilled water and swirl the flask. Add 74 mL of pyridine and mix. Add 15 mL of conc. HCl mix until the barbituric acid is dissolved. Dilute to 1 liter with distilled water. Store at 4°C.
- 7.4.4 Sampler Wash: Dissolve 10 g of NaOH in distilled water and dilute to 1 liter.

8. Procedure

8.1 Distillation

- 8.1.1 Accurately weigh a representative 1-5 g portion of wet sample and transfer it to a boiling flask. Add 500 mL of distilled water. Shake or stir the sample so that it is dispersed.

- 8.1.2 Add 50 mL of sodium hydroxide (7.1.1) to the absorbing tube and dilute if necessary with distilled water to obtain an adequate depth of liquid in the absorber. Connect the boiling flask, condenser, absorber, and trap in the train.
- 8.1.3 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately one bubble of air per second enters the boiling flask through the air inlet tube.

NOTE: The bubble rate will not remain constant after the reagents have been added and while heat is being applied to the flask. It will be necessary to readjust the air rate occasionally to prevent the solution in the boiling flask from backing up into the air inlet tube.

- 8.1.4 Slowly add 25 mL of conc. sulfuric acid (7.1.4) through the air inlet tube. Rinse the tube with distilled water and allow the airflow to mix the flask contents for 3 minutes. Pour 20 mL of magnesium chloride solution (7.1.5) into the air inlet and wash down with a stream of water.
- 8.1.5 Heat the solution to boiling, taking care to prevent the solution from backing up and overflowing into the air inlet tube. Reflux for one hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, disconnect absorber and close off the vacuum source.
- 8.1.6 Drain the solution from the absorber into a 250 mL volumetric flask and bring up to volume with distilled water washings from the absorber tube.

8.2 Titrimetric Determination (Option A)

- 8.2.1 If the sample contains more than 1 mg of CN, transfer the distillate, or a suitable aliquot diluted to 250 mL, to a 500 mL Erlenmeyer flask. Add 10-12 drops of the benzalrhodanine indicator.
- 8.2.2 Titrate with standard silver nitrate to the first change in color from yellow to brownish-pink. Titrate a distilled water blank using the same amount of sodium hydroxide and indicator as in the sample.
- 8.2.3 The analyst should familiarize himself with the end point of the titration and the amount of indicator to be used before actually titrating the samples. A 5 or 10 mL microburet may be conveniently used to obtain a more precise titration.

8.3 Manual Spectrophotometric Determination (Option B)

8.3.1 Withdraw 50 mL or less of the solution from the flask and transfer to a 100 mL volumetric flask. If less than 50 mL is taken, dilute to 50 mL with 0.25 N sodium hydroxide solution (7.2.6). Add 15.0 mL of sodium phosphate solution (7.3.2) and mix.

8.3.1.1 Pyridine-barbituric acid method: Add 2 mL of Chloramine-T (7.3.2) and mix. After 1 to 2 minutes, add 5 mL of pyridine-barbituric acid solution (7.3.3.1) and mix. Dilute to mark with distilled water and mix again. Allow 8 minutes for color development then read absorbance at 578 nm in a 1 cm cell within 15 minutes.

8.3.1.2 Pyridine-pyrazolone method: Add 0.5 mL of chloramine-T (7.3.2) and mix. After 1 to 2 minutes add 5 mL of pyridine-pyrazolone solution (7.3.3.2) and mix. Dilute to mark with distilled water and mix again. After 40 minutes read absorbance at 620 nm in a 1 cm cell.

NOTE: More than 0.5 mL of chloramine-T will prevent the color from developing with pyridine-pyrazolone.

8.3.2 Prepare a minimum of three standards and a blank by pipetting suitable volumes of standard solution into 250 mL volumetric flasks.

NOTE: One calibration standard, must be made at the CRDL. To each standard add 50 mL of 1.25 N sodium hydroxide and dilute to 250 mL with distilled water. Standards must bracket the concentrations of the sample. If dilution is required, use the blank solution.

As an example, standard solutions could be prepared as follows:

<u>mL of Standard Solution</u> <u>(1.0 = 5 ug CN)</u>	<u>Conc. ug CN</u> <u>per 250 mL</u>
0	Blank
1.0	5
2.0	10
5.0	25
10.0	50
15.0	75
20.0	100

8.3.2.1 It is not imperative that all standards be distilled in the same manner as the samples. At least one standard (mid-range) must be distilled and compared to similar values on the curve to insure that the distillation technique is reliable. If the distilled standard does not

agree within +15% of the undistilled standards the operator should find and correct the cause of the apparent error before proceeding.

- 8.3.2.2 Prepare a standard curve by plotting absorbance of standard vs. cyanide concentrations (per 250 mL)

8.4 Semi-Automated Spectrophotometric Determination (Option C)

- 8.4.1 Set up the manifold as shown in Figure 3. Pump the reagents through the system until a steady baseline is obtained.

- 8.4.2 Calibration standards: Prepare a blank and at least three calibration standards over the range of the analysis. One calibration standard must be at the CRDL. For a working range of 0-200 ug/L, the following standards may be used:

<u>mL Standard Solution</u> <u>(7.2.3) diluted to 1 liter</u>	<u>Concentration</u> <u>ug CN/L</u>
0	0
4.0	20
10.0	50
20.0	100
30.0	150
40.0	200

Add 10 g of NaOH to each standard. Store at 4°C(±2°C).

- 8.4.3 Place calibration standards, blanks, and control standards in the sampler tray, followed by distilled samples, distilled duplicates, distilled standards, distilled spikes, and distilled blanks.

- 8.4.4 - When a steady reagent baseline is obtained and before starting the sampler, adjust the baseline using the appropriate knob on the colorimeter. Aspirate a calibration standard and adjust the STD CAL dial on the colorimeter until the desired signal is obtained. Record the STD CAL value. Reestablish the baseline and proceed to analyze calibration standards, blanks, control standards, distilled samples, and distilled QC audits.

9. Calculations

- 9.1 A separate determination of percent solids must be performed (see Part F).
- 9.2 The concentration of cyanide in the sample is determined as follows.

9.2.1 (Titration)

$$\text{CN, mg/kg} = \frac{(A - B) \times \frac{250 \text{ mL}}{\text{mL aliquot titrated}} \times 1000 \text{ g/kg}}{C \times \frac{\% \text{solids}}{100}}$$

WHERE: A - mL of AgNO_3 for titration of sample
(1 mL = 1 mg Ag)
B - mL of AgNO_3 for titration of blank
(1 mL = 1 mg Ag)
C - wet weight of original sample in g
(See 8.1.1)

AND: 250 mL = volume of distillate (See 8.1.6)
1000 g/kg = conversion factor g to kg
mL aliquot titrated (See 8.2.1)
% solids (see Part F)

9.2.2 (Manual Spectrophotometric)

$$\text{CN, mg/kg} = \frac{A \times \frac{50 \text{ mL}}{B}}{C \times \frac{\% \text{solids}}{100}}$$

WHERE: A - ug CN read from standard curve (per 250 mL)
B - mL of distillate taken for colorimetric
determination (8.3.1)
C - wet weight of original sample in g
(See 8.1.1)

AND: 50 mL = volume of standard taken for colorimetric
determination (See 8.3.1)
% solids (see Part F)

9.2.3 (Semi-Automated Spectrophotometric)

If the semi-automated method is used, measure the peak heights of the calibration standards (visually or using a data system) and calculate a linear regression equation. Apply the equation to the samples and QC audits to determine the cyanide concentration in the distillates.

$$\text{CN, mg/kg} = \frac{A \times .25}{C \times \frac{\% \text{solids}}{100}}$$

WHERE: A - ug/L determined from standard curve
C - wet weight of original sample in g
(See 8.1.1)

AND: .25 - conversion factor for distillate final
volume (See 8.1.6)
% solids (see Part F)

Bibliography

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2. Methods for "Chemical Analysis of Water and Wastes", March 1979. EPA Publication #600/4-79-02.
3. "Operation Manual for Technicon Auto Analyzer IIC System", 1980. Technical publication #TA9-0460-00. Technicon Industrial Systems, Tarrytown, NY, 10591.
4. "Users Guide for the Continuous Flow Analyzer Automation System", ESL, U.S. EPA, Cincinnati, Ohio (1981).
5. "Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue," USEPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, August 1977, Revised October 1980.
6. Op. cit. (#5), Methods 335.2, modified (by committee).

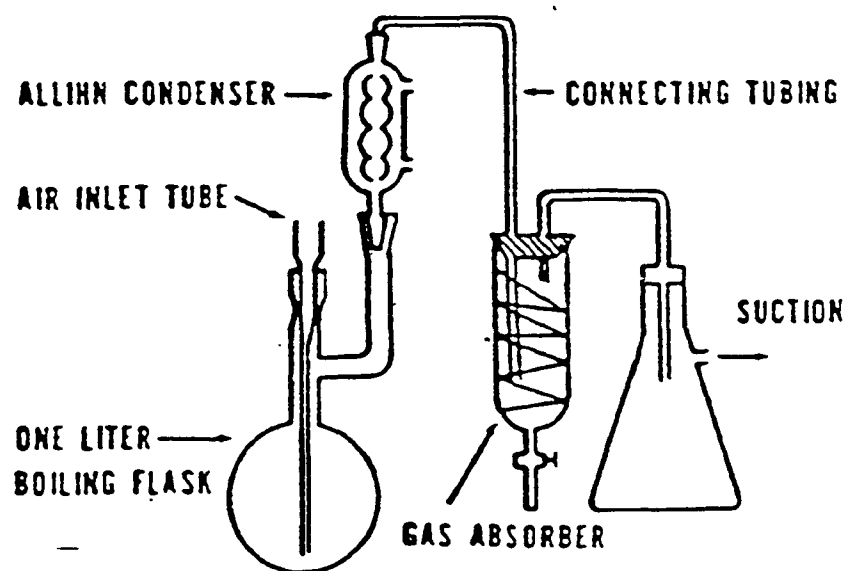


Figure 1. Cyanide distillation apparatus
D-80

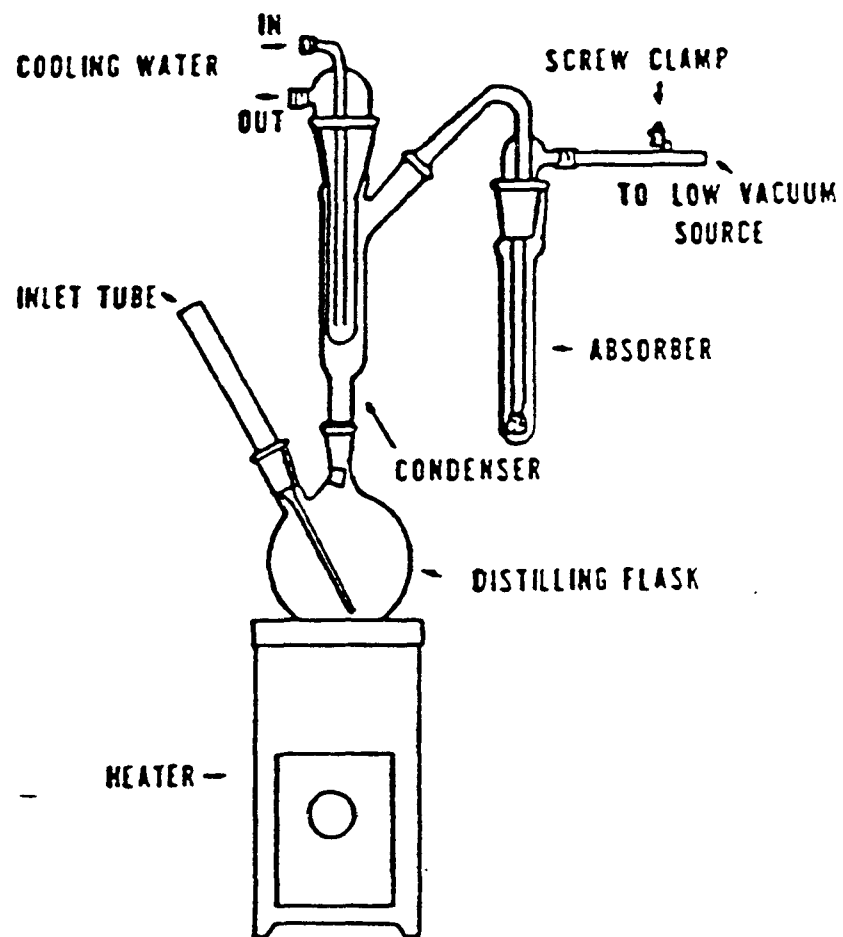


Figure 2. Cyanide distillation apparatus
D-81

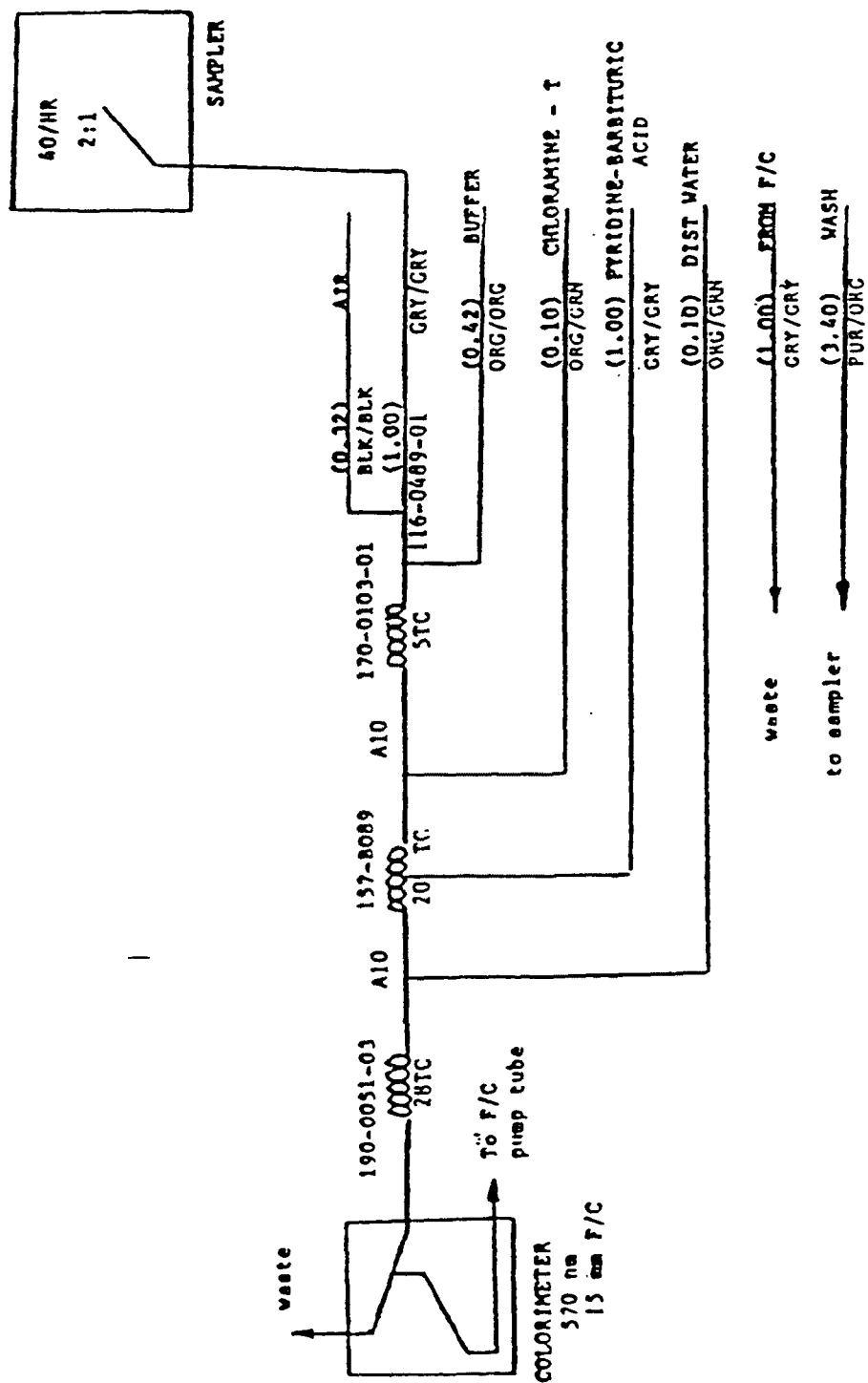


Figure 3. Cyanide Manifold
D-82

PART F - PERCENT SOLIDS DETERMINATION PROCEDURE

1. Immediately following the weighing of the sample to be processed for analysis (see Section III, Part B- Soil/Sediment Sample Preparation), add 5-10 g of sample to a tared weighing dish. Weigh and record the weight to the nearest 0.01 g.
2. Place weighing dish plus sample, with the cover tipped to allow for moisture escape, in a drying oven maintained at 103-105°C. Sample handling and drying should be conducted in a well-ventilated area.
3. Dry the sample overnight (12-24 hours) but no longer than 24 hours. If dried less than 12 hours, it must be documented that constant weight was attained.* Remove the sample from the oven and cool in a dessicator with the weighing dish cover in place before weighing. Weigh and record weight to nearest 0.01 g. Do not analyze the dried sample.
4. Duplicate percent solids determinations are required at the same frequency as are other analytical determinations. Duplicate results are to be recorded on FORM VI-IN.
5. For the duplicate percent solids determination, designate one sample aliquot as the "original" sample and the other aliquot as the "duplicate" sample. Calculate dry weight using the results of the "original" sample aliquot.
6. Calculate percent solids by the formula below. The value thus obtained will be reported on the appropriate FORM I-IN and, where applicable, FORM VI-IN. This value will be used for calculating analytical concentration on a dry weight basis.

$$\% \text{ Solids} = \frac{\text{Sample Dry Weight}}{\text{Sample Wet Weight}} \times 100$$

*For the purpose of paragraph 3, drying time is defined as the elapsed time in the oven; thus raw data must record time in and out of the oven to document the 12 hour drying time minimum. In the event it is necessary to demonstrate the attainment of constant weight, data must be recorded for a minimum of two repetitive weigh/dry/dessicate/weigh cycles with a minimum of 1 hour drying time in each cycle. Constant weight would be defined as a loss in weight of no greater than 0.01 g between the start weight and final weight of the last cycle.

PART G - ALTERNATE METHODS (CATASTROPHIC ICP FAILURE)⁺

<u>Analyte</u>	<u>Page No.</u>
Aluminum - Method 202.2 CLP-M*, Furnace AA	D-86
Barium - Method 208.2 CLP-M, Furnace AA	D-87
Cobalt - Method 219.2 CLP-M, Furnace AA	D-88
Copper - Method 220.2 CLP-M, Furnace AA	D-89
Iron - Method 236.2 CLP-M, Furnace AA	D-90
Manganese - Method 243.2 CLP-M, Furnace AA	D-91
Nickel - Method 249.2 CLP-M, Furnace AA	D-92
Vanadium - Method 286.2 CLP-M, Furnace AA	D-93
Zinc - Method 289.2 CLP-M, Furnace AA	D-94
Aluminum - Method 202.1 CLP-M, Flame AA	D-96
Antimony - Method 204.1 CLP-M, Flame AA	D-98
Barium - Method 208.1 CLP-M, Flame AA	D-99
Beryllium - Method 210.1 CLP-M, Flame AA	D-100
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Silver - Method 272.1 CLP-M, Flame AA	D-110
Thallium - Method 279.1 CLP-M, Flame AA	D-111
Vanadium - Method 286.1 CLP-M, Flame AA	D-112
Zinc - Method 289.1 CLP-M, Flame AA	D-113

⁺Furnace AA Methods are from "Methods for Chemical Analysis of Water and Wastes", (EPA-600/4-79-02), March 1979, as modified for use in the Contract Laboratory Program (CLP). Flame AA (Flame Technique) Methods are from "Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue," USEPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, August 1977, Revised October 1980, as modified for use in the CLP.

*CLP-M Modified for the Contract Laboratory Program.

CONDITIONS FOR USE OF ALTERNATE METHODS

The methods contained in Part G may be used only if all of the following conditions are met:

- 1) Catastrophic failure of ICP occurs,
- 2) Project Officer authorization for use of alternate methods is granted, and
- 3) The IDLs for the instrumentation have been determined, as per Exhibit E, within the current calendar quarter.

ALUMINUM*

Method 202.2 CLP-M** (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 20-200 ug/L
Approximate Detection Limit: 3 ug/L

Preparation of Standard Solution

1. Stock solution: Prepare as described under AA Flame Technique (Method 202.1 CLP-M).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C.
2. Ashing Time and Temp: 30 sec @ 1300°C.
3. Atomizing Time and Temp: 10 sec @ 2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 309.3 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only.
2. Background correction is required.
3. It has been reported that chloride ion and that nitrogen used as a purge gas suppress the aluminum signal. Therefore the use of halide acids and nitrogen as a purge gas should be avoided.
4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (Exhibit E).
5. If method of standard addition is required, follow the procedure given in Exhibit E.

*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

BARIUM*

Method 208.2 CLP-M** (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 10-200 ug/L

Approximate Detection Limit: 2 ug/L

Preparation of Standard Solution

1. Stock solution: Prepare as described under AA Flame Technique (Method 208.1 CLP-M).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°.
2. Ashing Time and Temp: 30 sec @ 1200°C.
3. Atomizing Time and Temp: 10 sec @ 2800°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 553.6 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and pyrolytic graphite and are to be used as guidelines only.
2. The use of halide acid should be avoided.
3. Because of possible chemical interaction, nitrogen should not be used as a purge gas.
4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
5. If method of standard addition is required, follow the procedure given in Exhibit E.

*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

COBALT*

Method 219.2 CLP-M** (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 5-100 ug/L

Approximate Detection Limit: 1 ug/L

Preparation of Standard Solution

1. Stock solution: Prepare as described under AA Flame Technique (Method 219.1 CLP-M).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C.
2. Ashing Time and Temp: 30 sec @ 900°C.
3. Atomizing Time and Temp: 10 sec @ 2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 240.7 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required.
3. Nitrogen may also be used as the purge gas but with reported low sensitivity.
4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
5. If method of standard addition is required, follow the procedure given in Exhibit E.

*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

COPPER*

Method 220.2 CLP-M** (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 5-100 ug/L
Approximate Detection Limit: 1 ug/L

Preparation of Standard Solution

1. Stock solution: Prepare as described under AA Flame Technique (Method 220.1 CLP-M).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C.
2. Ashing Time and Temp: 30 sec @ 900°C.
3. Atomizing Time and Temp: 10 sec @ 2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 324.7 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. Background correction is required.
3. Nitrogen may also be used as the purge gas.
4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
5. If method of standard addition is required, follow the procedure given in Exhibit E.

*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

IRON*

Method 236.2 CLP-M** (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 5-100 ug/L

Approximate Detection Limit: 1 ug/L

Preparation of Standard Solution

1. Stock solution: Prepare as described under AA Flame Technique (Method 236.1 CLP-M).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C.
2. Ashing Time and Temp: 30 sec @ 1000°C.
3. Atomizing Time and Temp: 10 sec @ 2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 248.3 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required.
3. Nitrogen may also be used as the purge gas.
4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
5. If method of standard addition is required, follow the procedure given in Exhibit E.

*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

MANGANESE*

Method 243.2 CLP-M** (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 1-30 ug/L

Approximate Detection Limit: 0.2 ug/L

Preparation of Standard Solution

1. Stock solution: Prepare as described under AA Flame Technique (Method 243.1 CLP-M).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C.
2. Ashing Time and Temp: 30 sec @ 1000°C.
3. Atomizing Time and Temp: 10 sec @ 2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 279.5 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required.
3. Nitrogen may also be used as the purge gas.
4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
5. If method of standard addition is required, follow the procedure given in Exhibit E.

*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

NICKEL*

Method 249.2 CLP-M** (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 5-100 ug/L

Approximate Detection Limit: 1 ug/L

Preparation of Standard Solution

1. Stock solution: Prepare as described under AA Flame Technique (Method 249.1 CLP-M).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C.
2. Ashing Time and Temp: 30 sec @ 900°C.
3. Atomizing Time and Temp: 10 sec @ 2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 232.0 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required.
3. Nitrogen may also be used as the purge gas.
4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
5. If method of standard addition is required, follow the procedure given in Exhibit E.

*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

VANADIUM*

Method 286.2 CLP-M** (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 10-200 ug/L

Approximate Detection Limit: 4 ug/L

Preparation of Standard Solution

1. Stock solution: Prepare as described under AA Flame Technique (Method 286.1 CLP-M).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions."
3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C.
2. Ashing Time and Temp: 30 sec @ 1400°C.
3. Atomizing Time and Temp: 15 sec @ 2800°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 318.4 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required.
3. Because of possible chemical interaction, nitrogen should not be used as the purge gas.
4. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Exhibit E).
5. If method of standard addition is required, follow the procedure given in Exhibit E.

*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

ZINC*

Method 289.2 CLP-M** (Atomic Absorption, Furnace Technique)

Optimum Concentration Range: 0.2-4 ug/L

Approximate Detection Limit: 0.05 ug/L

Preparation of Standard Solution

1. Stock solution: Prepare as described under AA Flame Technique (Method 289.1 CLP-M).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec @ 125°C.
2. Ashing Time and Temp: 30 sec @ 400°C.
3. Atomizing Time and Temp: 10 sec @ 2500°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 213.9 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is required.
3. Nitrogen may also be used as the purge gas.
4. The analysis of zinc by the graphite furnace is extremely sensitive and very subject to contamination from the work area, reagents, and pipette tips. Since all these factors affect the precision and accuracy, zinc should be analyzed by the direct aspiration procedure whenever possible.
5. For every sample analyzed, verification is necessary to determine that

*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

method of standard addition is not required (see Exhibit E).

6. If method of standard addition is required, follow the procedure given in Exhibit E.

ALUMINUM*

Method 202.1 CLP-M** (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 5-50 mg/L using a wavelength of 309.3 nm

Sensitivity: 1 mg/L

Approximate Detection Limit: 0.1 mg/L

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1,000 g of aluminum metal analytical reagent grade). Add 15 mL of conc. HCl and 5 mL conc. HNO₃ to the metal, cover the beaker and warm gently. When solution is complete, transfer quantitatively to a liter volumetric flask and make up to volume with deionized distilled water. 1 mL = 1 mg Al (1000 mg/L).
2. Potassium Chloride Solution: Dissolve 95 g potassium chloride (KCl) in deionized distilled water and make up to 1 liter.
3. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation. To each 100 mL of standard and sample alike add 2.0 mL potassium chloride solution.

Instrument Parameters (General)

1. Aluminum hollow cathode lamp
2. Wavelength: 309.3 nm
3. Fuel: Acetylene
4. Oxidant: Nitrous oxide
5. Type of flame: Fuel rich

Interferences

1. Aluminum is partially ionized in the nitrous oxide-acetylene flame. This problem may be controlled by the addition of an alkali metal (potassium, 1000 ug/mL) to both sample and standard solutions.

*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

Notes

1. The following may also be used:
 - 308.2 nm Relative Sensitivity 1
 - 396.2 nm Relative Sensitivity 2
 - 394.4 nm Relative Sensitivity 2.5
2. For concentrations of aluminum below 0.3 mg/L, use of Furnace Technique. (Method 202.2 CLP-M) is recommended.

ANTIMONY*

Method 204.1 CLP-M** (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 1-40 mg/L using a wavelength of 217.6 nm

Sensitivity: 0.5 mg/L

Approximate Detection Limit: 0.2 mg/L

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 2.7426 g of antimony potassium tartrate (analytical reagent grade) and dissolve in deionized distilled water. Dilute to 1 liter with deionized distilled water. 1 mL = 1 mg Sb (1000 mg/L).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrumental Parameters (General)

1. Antimony hollow cathode lamp
2. Wavelength: 217.6 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Fuel lean

Interferences

1. In the presence of lead (1000 mg/L), a special interference may occur at the 217.6 nm resonance line. In this case the 231.1 nm antimony line should be used.
2. Increasing acid concentrations decrease antimony absorption. To avoid this effect, the acid concentration in the samples and in the standards must be matched.

Notes

1. For concentrations of antimony below 0.35 mg/L, use of the Furnace Technique (Method 204.2 CLP-M) is recommended.

*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

BARIUM*

Method 208.1 CLP-M** (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 1-20 mg/L using a wavelength of 553.6 nm
Sensitivity: 0.4 mg/L
Approximate Detection Limit: 0.1 mg/L

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.7787 g of barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, analytical reagent grade) in deionized distilled water and dilute to liter. 1 mL = 1 mg Ba (1000 mg/L).
2. Potassium chloride solution: Dissolve 95 g potassium chloride, KCl, in deionized distilled water and make up to 1 liter.
3. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. To each 100 mL of standard and sample alike add 2.0 mL potassium chloride solution. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrumental Parameters (General)

1. Barium hollow cathode lamp
2. Wavelength: 553.6 nm
3. Fuel: Acetylene
4. Oxidant: Nitrous oxide
5. Type of flame: Fuel rich

Interferences

1. The use of a nitrous oxide-acetylene flame virtually eliminates chemical interference; however, barium is easily ionized in this flame and potassium must be added (1000 mg/L) to standards and samples alike to control this effect.
2. If the nitrous oxide flame is not available and acetylene-air is used, phosphate, silicon and aluminum will severely depress the barium absorbance. This may be overcome by the addition of 2000 mg/L lanthanum.

Notes

1. For concentrations of barium below 0.2 mg/L, use of the Furnace Technique (Method 208.2 CLP-M) is recommended.

*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

BERYLLIUM*

Method 210.1 CLP-M** (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.052 mg/L using a wavelength of 234.9 nm

Sensitivity: 0.025 mg/L

Approximate Detection Limit: 0.005 mg/L

Preparation of Standard Solution

1. Stock Solution: Dissolve 11.6586 g of beryllium sulfate, BeSO_4 , in deionized distilled water containing 2 mL conc. nitric acid and dilute to 1 liter. 1 mL = 1 mg Be (1000 mg/L).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrumental Parameters (General)

1. Beryllium hollow cathode lamp
2. Wavelength: 234.9 nm
3. Fuel: Acetylene
4. Oxidant: Nitrous oxide
5. Type of flame: Fuel rich

Interferences

1. Sodium and silicon at concentrations in excess of 1000 mg/L have been found to severely depress the beryllium absorbance.
2. Bicarbonate ion is reported to interfere; however, its effect is eliminated when samples are acidified to a pH of 1.5.
3. Aluminum at concentrations of 500 $\mu\text{g/L}$ is reported to depress the sensitivity of beryllium [Spectrochim Acta 22, 1325 (1966)].

Notes

1. For concentrations of beryllium below 0.02 mg/L, use of the Furnace Technique (Method 210.2 CLP-M) is recommended.

*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

CADMIUM*

Method 213.1 CLP-M** (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.052 mg/L using a wavelength of 228.8 nm

Sensitivity: 0.025 mg/L

Approximate Detection Limit: 0.005 mg/L

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 2.282 g of cadmium sulfate ($3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$, analytical reagent grade) and dissolve in deionized distilled water. Make up to 1 liter with deionized distilled water. 1 mL = 1 mg Cd (1000 mg/L).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrumental Parameters (General)

1. Cadmium hollow cathode lamp
2. Wavelength: 228.8 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. For concentrations of cadmium below 20 ug/L, use of the Furnace Technique, Method 213.2 CLP-M is recommended.

*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

CHROMIUM*

Method 218.1 CLP-M** (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.5-10 mg/L using a wavelength of 357.9 nm

Sensitivity: 0.25 mg/L

Approximate Detection Limit: 0.05 mg/L

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.923 g of chromium trioxide (CrO_3 , reagent grade) in deionized distilled water. When solution is complete, acidify with redistilled HNO_3 and dilute to 1 liter with deionized distilled water. 1 mL = 1 mg Cr (1000 mg/L).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Chromium hollow cathode lamp
2. Wavelength: 357.9 nm
3. Fuel: Acetylene
4. Oxidant: Nitrous oxide
5. Type of flame: Fuel rich

Notes

1. The following wavelengths may also be used:
359.3 nm Relative Sensitivity 1.4
425.4 nm Relative Sensitivity 2
427.5 nm Relative Sensitivity 3
428.9 nm Relative Sensitivity 4
2. The fuel rich air-acetylene flame provides greater sensitivity but is subject to chemical and matrix interference from iron, nickel, and other metals. If the analysis is performed in a lean flame the interference can be lessened but the sensitivity will also be reduced.
3. The suppression of both Cr (III) and Cr (VI) absorption by most interfering ions in fuel rich air-acetylene flames is reportedly controlled by the addition of 1% ammonium bifluoride in 0.2% sodium sulfate [Talanta 20, 631 (1973)]. A 1% oxine solution is also reported to be useful.
4. For concentrations of chromium between 50 and 200 ug/L where the air-acetylene flame cannot be used or for concentrations below 50 ug/L, use of the Furnace Technique (Method 218.2 CLP-M) is recommended.

*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

COBALT*

Method 219.1** CLP-M (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.5-5 mg/L using a wavelength of 240.7 nm

Sensitivity: 0.2 mg/L

Approximate Detection Limit: 0.05 mg/L

Preparation of Standard Solution

1. Stock Solution: Dissolve 4.307 g of cobaltous chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ analytical reagent grade), in deionized distilled water. Add 10 mL of concentrated nitric acid and dilute to 1 liter with deionized distilled water. 1 mL = 1 mg Co (1000 mg/L).
2. Prepare dilutions of the stock cobalt solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrument Parameters (General)

1. Cobalt hollow cathode lamp
2. Wavelength: 240.7 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. For concentrations of cobalt below 100 ug/L use of the Furnace Technique (Method 219.2 CLP-M) is recommended.

*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

COPPER*

Method 220.1 CLP-M** (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.2-5 mg/L using a wavelength of 324.7 nm

Sensitivity: 0.1 mg/L

Approximate Detection Limit: 0.02 mg/L

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 100 g of electrolyte copper (analytical reagent grade). Dissolve in 5 mL redistilled HNO_3 and make up to 1 liter with deionized distilled water. Final concentration is 1 mg Cu per mL (1000 mg/L).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrumental Parameters (General)

1. Copper hollow cathode lamp
2. Wavelength: 324.7 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. For concentrations of copper below 50 ug/L use of the Furnace Technique (Method 220.2 CLP-M) is recommended.
2. Numerous absorption lines are available for the determination of copper. By selecting a suitable absorption wavelength, copper samples may be analyzed over a very wide range of concentrations. The following lines may be used:

327.4 nm Relative Sensitivity 2
216.5 nm Relative Sensitivity 7
222.5 nm Relative Sensitivity 20

*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

IRON*

Method 236.1 CLP-M** (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.3-5 mg/L using a wavelength of 248.3 nm

Sensitivity: 0.12 mg/L

Approximate Detection Limit: 0.03 mg/L

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.000 g of pure iron wire (analytical reagent grade) and dissolve in 5 mL redistilled HNO_3 , warming if necessary. When solution is complete, make up to 1 liter with deionized distilled water. 1 mL = 1 mg Fe (1000 mg/L).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrumental Parameters (General)

1. Iron hollow cathode lamp
2. Wavelength: 248.3 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. The following wavelengths may also be used:
248.8 nm Relative Sensitivity 2
271.9 nm Relative Sensitivity 4
302.1 nm Relative Sensitivity 5
252.7 nm Relative Sensitivity 6
372.0 nm Relative Sensitivity 10
2. For concentrations of iron below 0.05 mg/L use of the Furnace Technique (Method 236.2 CLP-M) is recommended.

*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

LEAD*

Method 239.1 CLP-M** (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 1-20 mg/L using a wavelength of 283.3 nm

Sensitivity: 0.5 mg/L

Approximate Detection Limit: 0.1 mg/L

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.599 g of lead nitrate, $\text{Pb}(\text{NO}_3)_2$ (analytical reagent grade), and dissolve in deionized distilled water. When solution is complete acidify with 10 mL redistilled HNO_3 and dilute to 1 liter with deionized distilled water. 1 mL = 1 mg Pb (1000 mg/L).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrumental Parameters (General)

1. Lead hollow cathode lamp
2. Wavelength: 283.3 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. The analysis of this metal is exceptionally sensitive to turbulence and absorption bands in the flame. Therefore, some care should be taken to position the light beam in the most stable, center portion of the flame. To do this, first adjust the burner to maximize the absorbance reading with a lead standard. Then, aspirate a water blank and make minute adjustments in the burner alignment to minimize the signal.
2. The concentrations of lead below 200 ug/L use of the Furnace Technique (Method 239.2 CLP-M) is recommended.
3. The following wavelengths may also be used:
217.0 nm Relative Sensitivity 0.4
261.4 nm Relative Sensitivity 10

*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

MANGANESE*

Method 243.1 CLP-M** (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.1-3 mg/L using a wavelength of 279.5 nm

Sensitivity: 0.05 mg/L

Approximate Detection Limit: 0.01 mg/L

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.000 g of manganese metal (analytical reagent grade), and dissolve in 10 mL redistilled HNO_3 . When solution is complete, dilute to 1 liter with 1% (v/v) HCl. 1 mL = 1 mg Mn (1000 mg/L).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrumental Parameters (General)

1. Manganese hollow cathode lamp
2. Wavelength: 279.5 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. For concentrations of manganese below 25 ug/L, use of the Furnace Technique (Method 243.2 CLP-M) is recommended.
2. The following line may also be used: 403.1 nm Relative Sensitivity 10.

*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

NICKEL*

Method 249.1 CLP-M** (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.3-5 mg/L using a wavelength of 232.0 nm

Sensitivity: 0.15 mg/L

Approximate Detection Limit: 0.04 mg/L

Preparation of Standard Solution

1. Stock Solution: Dissolve 4.953 g of nickel nitrate, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (analytical reagent grade) in deionizing distilled water. Add 10 mL of conc. nitric acid and dilute to 1 liter deionized distilled water. 1 mL = 1 mg Ni (1000 mg/L).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrumental Parameters (General)

1. Nickel hollow cathode lamp
2. Wavelength: 232.0 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Interferences

1. The 352.4 nm wavelength is less susceptible to spectral interference and may be used. The calibration curve is more linear at this wavelength; however, there is some loss of sensitivity.

Notes

1. For concentrations of nickel below 100 ug/L, use of the Furnace Technique (Method 249.2 CLP-M) is recommended.

*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

SILVER*

Method 272.1 CLP-M** (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.1-4 mg/L using a wavelength of 328.1 nm
Sensitivity: 0.06 mg/L
Approximate Detection Limit: 0.01 mg/L

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.575 g of AgNO_3 , (analytical reagent grade) in deionized distilled water, add 10 mL conc. HNO_3 and make up to 1 liter. 1 mL = 1 mg Ag (1000 mg/L).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.
3. Iodine Solution, 1 N: Dissolve 20 grams of potassium iodide, KI (analytical reagent grade) in 50 mL of deionized distilled water, add 12.7 grams of iodine, I_2 , (analytical reagent grade) and dilute to 100 mL. Store in a brown bottle.
4. Cyanogen Iodide (CNI) Solution: To 50 mL of deionized distilled water add 4.0 mL conc. NH_4OH , 6.5 grams KCN, and 5.0 mL of 1.0 N I_2 solution. Mix and dilute to 100 mL with deionized distilled water. Fresh solution should be prepared every two weeks. (1)

Instrumental Parameters (General)

1. Silver hollow cathode lamp
2. Wavelength: 328.1 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. For concentrations of silver below 30 ug/L, use of the Furnace Technique (Method 272.2 CLP-M) is recommended.
2. Silver nitrate standards are light sensitive. Dilutions of the stock should be discarded after use as concentrations below 10 mg/L are not stable over long periods of time.

*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

3. If absorption to container walls or the formation of AgCl is suspected, make the sample basic using conc. NH_4OH and add 1 mL of (CNI) solution per 100 mL of sample. Mix the sample and allow to stand for 1 hour before proceeding with the analysis.(1)
4. The 338.2 nm wavelength may also be used. This has a relative sensitivity of 2.

References

1. "The Use of Cyanogen Iodide (CNI) as a Stabilizing Agent for Silver in Photographic Processing Effluent Sample", Owerbach, Daniel, Photographic Technology Division, Eastman Kodak Company, Rochester, N.Y. 14650.

THALLIUM*

Method 279.1 CLP-M** (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 1-20 mg/L using a wavelength of 276.8 nm

Sensitivity: 0.5 mg/L

Approximate Detection Limit: 0.1 mg/L

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.303 g of thallium nitrate, $TlNO_3$ (analytical reagent grade) in deionized distilled water. Add 10 mL of conc. nitric acid and dilute to 1 liter with deionized distilled water. 1 mL = 1 mg Tl (1000 mg/L).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using nitric acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrumental Parameters (General)

1. Thallium hollow cathode lamp
2. Wavelength: 276.8 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. For concentrations of thallium below 0.2 mg/L, use of the Furnace Technique (Method 279.2 CLP-M) is recommended.

*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

VANADIUM*

Method 286.1 CLP-M** (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 2-100 mg/L using a wavelength of 318.4 nm

Sensitivity: 0.8 mg/L

Approximate Detection Limit: 0.2 mg/L

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.7854 g of vanadium pentoxide, V_2O_5 (analytical reagent grade) in 10 mL of conc. nitric acid and dilute to 1 liter with deionized distilled water. 1 mL = 1 mg V (1000 mg/L).
2. Aluminum nitrate solution: Dissolve 139 g aluminum nitrate, $Al(NO_3)_3 \cdot 9H_2O$, in 150 mL of deionized distilled water; heat to effect solution. Allow to cool and make up to 200 mL.
3. Prepare dilutions of the stock vanadium solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation. To each 100 mL of standard and sample alike, add 2 mL of the aluminum nitrate solution.

Instrumental Parameters (General)

1. Vanadium hollow cathode lamp
2. Wavelength: 318.4 nm
3. Fuel: Acetylene
4. Oxidant: Nitrous Oxide
5. Type of flame: Fuel rich

Interferences —

1. It has been reported that high concentrations of aluminum and titanium increase the sensitivity of vanadium. This interference can be controlled by adding excess aluminum (1000 ppm) to both samples and standards. [Talanta 15, 871 (1968)].

Notes

1. For concentrations of vanadium below 0.5 mg/L, use of the Furnace Technique (Method 282.6 CLP-M) is recommended.

*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

ZINC*

Method 289.1 CLP-M** (Atomic Absorption, Flame Technique)

Optimum Concentration Range: 0.05-1 mg/L using a wavelength of 213.9 nm

Sensitivity: 0.02 mg/L

Approximate Detection Limit: 0.005 mg/L

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.00 g of zinc metal (analytical reagent grade) and dissolve cautiously in 10 mL HNO_3 . When solution is complete make up to 1 liter with deionized distilled water. 1 mL = 1 mg Zn (1000 mg/L).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

Instrumental Parameters (General)

1. Zinc hollow cathode lamp
2. Wavelength: 213.9 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Notes

1. High levels of silicon may interfere.
2. The air-acetylene flame absorbs about 25% of the energy at the 213.9 nm line.
3. The sensitivity may be increased by the use of low-temperature flames.
4. Some container cap liners can be a source of zinc contamination. To circumvent or avoid this problem, the use of the polypropylene caps is recommended.
5. For concentrations of zinc below 0.01 mg/L, use of the Furnace Technique (Method 289.2 CLP-M) is recommended.

*This method may only be used under specified conditions.

**CLP-M Modified for the Contract Laboratory Program.

EXHIBIT E

QUALITY ASSURANCE/QUALITY CONTROL REQUIREMENTS

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SECTION I

GENERAL QA/QC PRACTICES

Standard laboratory practices for laboratory cleanliness as applied to glassware and apparatus must be adhered to. Laboratory practices with regard to reagents, solvents, and gases must also be adhered to. For additional guidelines regarding these general laboratory procedures, see Sections 4 and 5 of the Handbook for Analytical Quality Control in Water and Wastewater Laboratories EPA-600/4-79-019, USEPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, March 1979.

SECTION II

SPECIFIC QA/QC PROCEDURES

The quality assurance/quality control (QA/QC) procedures defined herein must be used by the Contractor when performing the methods specified in Exhibit D. When additional QA/QC procedures are specified in the methods in Exhibit D, the Contractor must also follow these procedures.

NOTE: The cost of performing all QA/QC procedures specified in this Statement of Work is included in the price of performing the bid lot, except for duplicate, spike, and laboratory control sample analyses, which shall be considered separate sample analyses.

The purpose of this document is to provide a uniform set of procedures for the analysis of inorganic constituents of samples, documentation of methods and their performance, and verification of the sample data generated. The program will also assist laboratory personnel in recalling and defending their actions under cross examination if required to present court testimony in enforcement case litigation.

The primary function of the QA/QC program is the definition of procedures for the evaluation and documentation of sampling and analytical methodologies and the reduction and reporting of data. The objective is to provide a uniform basis for sample collection and handling, instrument and methods maintenance, performance evaluation, and analytical data gathering and reporting. Although it is impossible to address all analytical situations in one document, the approach taken here is to define minimum requirements for all major steps relevant to any inorganic analysis. In many instances where methodologies are available, specific quality control procedures are incorporated into the method documentation (Exhibit D). Ideally, samples involved in enforcement actions are analyzed only after the methods have met the minimum performance and documentation requirements described in this document.

The Contractor is required to participate in the Laboratory Audit and Intercomparison Study Program run by EPA EMSL-Las Vegas. The Contractor can expect to analyze two samples per calendar quarter during the contract period.

The Contractor must perform and report to SMO and EMSL/LV as specified in Exhibit B quarterly verification of instrument detection limits (IDL) by the method specified in Exhibit E, by type and model for each instrument used on this contract. All the IDLs must meet the CRDLs specified in Exhibit C. For ICP methods, the Contractor must also report, as specified in Exhibit B, linearity range verification, all interelement correction factors, wavelengths used, and integration times.

In this Exhibit, as well as other places within this Statement of Work, the term "analytical sample" is used in discussing the required frequency or placement of certain QA/QC measurements. The term "analytical sample" is defined in the glossary, Exhibit G. As the term is used, analytical sample includes all field samples, including Performance Evaluation samples, received from an external source, but it also includes all required QA/QC samples (matrix spikes, analytical/post-digestion

spikes, 'duplicates, serial dilutions, LCS, ICS, CRDL standards, preparation blanks and linear range analyses) except those directly related to instrument calibration or calibration verification (calibration standards, ICV/ICB, CCV/CCB). A "frequency of 10%" means once every 10 analytical samples. Note: Calibration verification samples (ICV/CCV) and calibration verification blanks (ICB/CCB) are not counted as analytical samples when determining 10% frequency.

In order for the QA/QC information to reflect the status of the samples analyzed, all samples and their QA/QC analysis must be analyzed under the same operating and procedural conditions.

If any QC measurement fails to meet contract criteria, the analytical measurement may not be repeated prior to taking the appropriate corrective action as specified in Exhibit E.

The Contractor must report all QC data in the exact format specified in Exhibits B and H.

This section outlines the minimum QA/QC operations necessary to satisfy the analytical requirements of the contract. The following QA/QC operations must be performed as described in this Exhibit:

1. Instrument Calibration
2. Initial Calibration Verification (ICV) and Continuing Calibration Verification (CCV)
3. CRDL Standards for AA (CRA) and ICP (CRI)
4. Initial Calibration Blank (ICB), Continuing Calibration Blank (CCB), and Preparation Blank (PB) Analyses
5. ICP Interference Check Sample (ICS) Analyses
6. Spike Sample Analysis (S)
7. Duplicate Sample Analysis (D)
8. Laboratory Control Sample (LCS) Analysis
9. IGP Serial Dilution Analysis (L)
10. Instrument Detection Limit (IDL) Determination
11. Interelement Corrections for ICP (ICP)
12. Linear Range Analysis (LRA)
13. Furnace AA QC Analyses

1. Instrument Calibration

Guidelines for instrumental calibration are given in EPA 600/4-79-020 and/or Exhibit D. Instruments must be calibrated daily or once every 24 hours and each time the instrument is set up. The instrument standardization date and time must be included in the raw data.

For atomic absorption systems, calibration standards are prepared by diluting the stock metal solutions at the time of analysis. Date and time of preparation and analysis must be given in the raw data.

Calibration standards must be prepared fresh each time an analysis is to be made and discarded after use. Prepare a blank and at least three calibration standards in graduated amounts in the appropriate range. One atomic absorption calibration standard must be at the CRDL except for mercury. The calibration standards must be prepared using the same type of acid or combination of acids and at the same concentration as will result in the samples following sample preparation.

Beginning with the blank, aspirate or inject the standards and record the readings. If the AA instrument configuration prevents the required 4-point calibration, calibrate according to instrument manufacturer's recommendations, and analyze the remaining required standards immediately after calibration. Results for these standards must be within $\pm 5\%$ of the true value. Each standards concentration and the calculations to show that the $\pm 5\%$ criterion has been met, must be given in the raw data. If the values do not fall within this range, recalibration is necessary.

The $\pm 5\%$ criteria does not apply to the atomic absorption calibration standard at the CRDL.

Calibration standards for AA procedures must be prepared as described in Exhibit D.

Baseline correction is acceptable as long as it is performed after every sample or after the continuing calibration verification and blank check; resloping is acceptable as long as it is immediately preceded and immediately followed by CCV and CCB. For cyanide and mercury, follow the calibration procedures outlined in Exhibit D. One cyanide calibration standard must be at the CRDL. For ICP systems, calibrate the instrument according to instrument manufacturer's recommended procedures. At least two standards must be used for ICP calibration. One of the standards must be a blank.

2. Initial Calibration Verification (ICV) and Continuing Calibration Verification (CCV)

a. Initial Calibration Verification (ICV)

Immediately after each of the ICP, AA and cyanide systems have been calibrated, the accuracy of the initial calibration shall be verified and documented for every analyte by the analysis of EPA Initial Calibration Verification Solution(s) at each wavelength used for analysis. When measurements exceed the control limits of Table 1-Initial and Continuing Calibration Verification Control Limits for Inorganic Analyses (in Exhibit E), the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified.

If the Initial Calibration Verification Solution(s) are not available from EPA, or where a certified solution of an analyte is not available from any source, analyses shall be conducted on an independent standard at a concentration other than that used for instrument calibration, but within the calibration range. An independent standard is defined as a standard composed of the analytes from a different source than those used in the standards for the instrument calibration.

For ICP, the Initial Calibration Verification Solution(s) must be run at each wavelength used for analysis. For CN, the initial calibration verification standard must be distilled. The Initial Calibration Verification for CN serves as a Laboratory Control Sample; thus it must be distilled with the batch of samples analyzed in association with that ICV. This means that an ICV must be distilled with each batch of samples analyzed and that the samples distilled with an ICV must be analyzed with that particular ICV. The values for the initial and subsequent continuing calibration verifications shall be recorded on FORM II-IN for ICP, AA, and cyanide analyses, as indicated.

b. Continuing Calibration Verification (CCV)

To ensure calibration accuracy during each analysis run, one of the following standards is to be used for continuing calibration verification and must be analyzed and reported for every wavelength used for the analysis of each analyte, at a frequency of 10% or every 2 hours during an analysis run, whichever is more frequent. The standard must also be analyzed and reported for every wavelength used for analysis at the beginning of the run and after the last analytical sample. The analyte concentrations in the continuing calibration standard must be one of the following solutions at or near the mid-range levels of the calibration curve:

1. EPA Solutions
2. NBS SRM 1643a
3. A Contractor-prepared standard solution

TABLE 1. INITIAL AND CONTINUING CALIBRATION VERIFICATION CONTROL LIMITS FOR INORGANIC ANALYSES

Analytical Method	Inorganic Species	% of True Value (EPA Set)	
		Low Limit	High Limit
ICP/AA	Metals	90	110
Cold Vapor AA	Mercury	80	120
Other	Cyanide	85	115

The same continuing calibration standard must be used throughout the analysis runs for a Case of samples received.

Each CCV analyzed must reflect the conditions of analysis of all associated analytical samples (the preceding 10 analytical samples or the preceding analytical samples up to the previous CCV). The duration of analysis, rinses and other related operations that may affect the CCV measured result may not be applied to the CCV to a greater extent than the extent applied to the associated analytical samples. For instance, the difference in time between a CCV analysis and the blank immediately following it as well as the difference in time between the CCV and the analytical sample immediately preceding it may not exceed the lowest difference in time between any two consecutive analytical samples associated with the CCV.

If the deviation of the continuing calibration verification is greater than the control limits specified in Table 1-Initial and Continuing Calibration Verification Control Limits for Inorganic Analyses, the analysis must be stopped, the problem corrected, the instrument must be recalibrated, the calibration verified and the reanalysis of preceding 10 analytical samples or all analytical samples analyzed since the last good calibration verification must be performed for the analytes affected. Information regarding the continuing verification of calibration shall be recorded on FORM II-IN for ICP, AA and cyanide as indicated.

3. CRDL Standards for ICP (CRI) and AA (CRA)

To verify linearity near the CRDL for ICP analysis, the Contractor must analyze an ICP standard (CRI) at two times the CRDL or two times the IDL, whichever is greater, at the beginning and end of each sample analysis run, or a minimum of twice per 8 hour working shift, whichever is more frequent, but not before Initial Calibration Verification. This standard must be run by ICP for every wavelength used for analysis, except those for Al, Ba, Ca, Fe, Mg, Na and K.

To verify linearity near the CRDL for AA analysis, the Contractor must analyze an AA standard (CRA) at the CRDL or the IDL, whichever is greater, at the beginning of each sample analysis run, but not before the Initial Calibration Verification.

Specific acceptance criteria for the two standards will be set by EPA in the future. In the interim, the Contractor must analyze and report these Standards on FORM II(PART 2)-IN.

4. Initial Calibration Blank (ICB), Continuing Calibration Blank (CCB), and Preparation Blank (PB) Analyses

a. Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB) Analyses

A calibration blank must be analyzed at each wavelength used for analysis immediately after every initial and continuing calibration verification, at a frequency of 10% or every 2 hours

during the run, whichever is more frequent. The blank must be analyzed at the beginning of the run and after the last analytical sample. Note: A CCB must be run after the last CCV that was run after the last analytical sample of the run. The results for the calibration blanks shall be recorded on FORM III-IN for ICP, AA and cyanide analyses, as indicated. If the magnitude (absolute value) of the calibration blank result exceeds the IDL, the result must be so reported in ug/L on FORM III-IN, otherwise report as IDL-U. If the absolute value blank result exceeds the CRDL (Exhibit C), terminate analysis, correct the problem, recalibrate, verify the calibration and reanalyze the preceding 10 analytical samples or all analytical samples analyzed since the last good calibration blank.

b. Preparation Blank (PB) Analysis

At least one preparation blank (or reagent blank), consisting of deionized distilled water processed through each sample preparation and analysis procedure (See Exhibit D, Section III), must be prepared and analyzed with every Sample Delivery Group, or with each batch¹ of samples digested, whichever is more frequent.

The first batch of samples in an SDG is to be assigned to preparation blank one, the second batch of samples to preparation blank two, etc. (see FORM III-IN). Each data package must contain the results of all the preparation blank analyses associated with the samples in that SDG.

This blank is to be reported for each SDG and used in all analyses to ascertain whether sample concentrations reflect contamination in the following manner:

- 1) If the absolute value of the concentration of the blank is less than or equal to the Contract Required Detection Limit (Exhibit C), no correction of sample results is performed.
- 2) If any analyte concentration in the blank is above the CRDL, the lowest concentration of that analyte in the associated samples must be 10x the blank concentration. Otherwise, all samples associated with the blank with the analyte's concentration less than 10x the blank concentration and above the CRDL, must be redigested and reanalyzed for that analyte (except for an identified aqueous soil field blank). The sample concentration is not to be corrected for the blank value.
- 3) If the concentration of the blank is below the negative CRDL, then all samples reported below 10x CRDL associated with the blank must be redigested and reanalyzed.

¹A group of samples prepared at the same time.

The values for the preparation blank must be recorded in ug/L for aqueous samples and in mg/Kg for solid samples on FORM III-IN for ICP, AA, and cyanide analyses.

5. ICP Interference Check Sample (ICS) Analysis

To verify interelement and background correction factors, the Contractor must analyze and report the results for the ICP Interference Check Samples at the beginning and end of each analysis run or a minimum of twice per 8 hour working shift, whichever is more frequent, but not before Initial Calibration Verification. The ICP Interference Check Samples must be obtained from EPA (EMSL/LV) if available and analyzed according to the instructions supplied with the ICS.

The Interference Check Samples consist of two solutions: Solution A and Solution AB. Solution A consists of the interferents, and Solution AB consists of the analytes mixed with the interferents. An ICS analysis consists of analyzing both solutions consecutively (starting with Solution A) for all wavelengths used for each analyte reported by ICP.

Results for the ICP analyses of Solution AB during the analytical runs must fall within the control limit of $\pm 20\%$ of the true value for the analytes included in the Interference Check Samples. If not, terminate the analysis, correct the problem, recalibrate the instrument, and reanalyze the analytical samples analyzed since the last good ICS. If true values for analytes contained in the ICS and analyzed by ICP are not supplied with the ICS, the mean must be determined by initially analyzing the ICS at least five times repetitively for the particular analytes. This mean determination must be made during an analytical run where the results for the previously supplied EPA ICS met all contract specifications. Additionally, the result of this initial mean determination is to be used as the true value for the lifetime of that solution (i.e., until the solution is exhausted).

If the ICP Interference Check Sample is not available from EPA, independent ICP Check Samples must be prepared with interferent and analyte concentrations at the levels specified in Table 2-Interferent and Analyte Elemental Concentrations Used for ICP Interference Check Sample. The mean value and standard deviation must be established by initially analyzing the Check Samples at least five times repetitively for each parameter on FORM IV-IN. Results must fall within the control limit of $\pm 20\%$ of the established mean value. The mean and standard deviation must be reported in the raw data. Results from the Interference Check Sample analyses must be recorded on FORM IV-IN for all ICP parameters.

TABLE 2. INTERFERENT AND ANALYTE ELEMENTAL CONCENTRATIONS USED FOR ICP INTERFERENCE CHECK SAMPLE

Analytes	(mg/L)	Interferents	(mg/L)
Ag	1.0	Al	500
Ba	0.5	Ca	500
Be	0.5	Fe	200
Cd	1.0	Mg	500
Co	0.5		
Cr	0.5		
Cu	0.5		
Mn	0.5		
Ni	1.0		
Pb	1.0		
V	0.5		
Zn	1.0		

6. Spike Sample Analysis (S)

The spike sample analysis is designed to provide information about the effect of the sample matrix on the digestion and measurement methodology. The spike is added before the digestion (i.e., prior to the addition of other reagents) and prior to any distillation steps (i.e., CN-). At least one spike sample analysis must be performed on each group of samples of a similar matrix type (i.e., water, soil) and concentration (i.e., low, medium) or for each Sample Delivery Group.²

If the spike analysis is performed on the same sample that is chosen for the duplicate sample analysis, spike calculations must be performed using the results of the sample designated as the "original sample" (see section 7, Duplicate Sample Analysis). The average of the duplicate results cannot be used for the purpose of determining percent recovery. Samples identified as field blanks cannot be used for spiked sample analysis. EPA may require that a specific sample be used for the spike sample analysis.

The analyte spike must be added in the amount given in Table 3-Spiking Levels for Spike Sample Analysis, for each element analyzed. If two analytical methods are used to obtain the reported values for the same element within a Sample Delivery Group (i.e. ICP, GFAA), spike samples must be run by each method used.

²EPA may require additional spike sample analysis, upon Project Officer request, for which the Contractor will be paid.

If the spike recovery is not at or within the limits of 75-125%, the data of all samples received associated with that spike sample and determined by the same analytical method must be flagged with the letter "N" on FORMs I-IN and V-IN. An exception to this rule is granted in situations where the sample concentration exceeds the spike concentration by a factor of four or more. In such an event, the data shall be reported unflagged even if the percent recovery does not meet the 75-125% recovery criteria.

For flame AA, ICP, and CN analyses, when the pre-digestion/pre-distillation spike recovery falls outside the control limits and the sample result does not exceed 4x the spike added, a post-digestion/post-distillation spike must be performed for those elements that do not meet the specified criteria (exception: Ag). Spike the unspiked aliquot of the sample at 2x the indigenous level or 2x CRDL, whichever is greater. Results of the post-digestion/post-distillation spike must be reported on FORM V(PART 2)-IN. Note: No post digest spike is required for Hg.

In the instance where there is more than one spike sample per matrix and concentration per method per SDG, if one spike sample recovery is not within contract criteria, flag all the samples of the same matrix, level, and method in the SDG. Individual component percent recoveries (%R) are calculated as follows:

$$\% \text{Recovery} = \frac{(\text{SSR} - \text{SR})}{\text{SA}} \times 100$$

Where, SSR - Spiked Sample Result
 SR - Sample Result
 SA - Spike Added

When sample concentration is less than the instrument detection limit, use SR = 0 only for purposes of calculating % Recovery. The spike sample results, sample results and % Recovery (positive or negative) must be reported on FORM V-IN for ICP, AA and cyanide analyses, as indicated.

The units for reporting spike sample results will be identical to those used for reporting sample results in FORM I-IN (i.e., ug/L for aqueous and mg/Kg dry weight basis for solid).

TABLE 3. SPIKING LEVELS FOR SPIKE SAMPLE ANALYSIS					
Element	For ICP/AA (ug/L)		For Furnace AA (ug/L)		Other ⁽¹⁾ (ug/L)
	Water	Soil ⁽²⁾	Water	Soil	
Aluminum	2,000	*			
Antimony	500	500	100	100	
Arsenic	2,000	2,000	40	40	
Barium	2,000	2,000			
Beryllium	50	50			
Cadmium	50	50	5	5	
Calcium	*	*			
Chromium	200	200			
Cobalt	500	500			
Copper	250	250			
Iron	1,000	*			
Lead	500	500	20	20	
Magnesium	*	*			
Manganese	500	500			
Mercury					1
Nickel	500	500			
Potassium	*	*			
Selenium	2,000	2,000	10	10	
Silver	50	50			
Sodium	*	*			
Thallium	2,000	2,000	50	50	
Vanadium	500	500			
Zinc	500	500			
Cyanide					100

NOTE: Elements without spike levels and not designated with an asterisk, must be spiked at appropriate levels.

¹Spiking level reported is for both water and soil/sediment matrices.

²The levels shown indicate concentrations in the final digestate of the spiked sample (200 mL final volume).

*No spike required.

7. Duplicate Sample Analysis (D)

One duplicate sample must be analyzed from each group of samples of a similar matrix type (i.e., water, soil) and concentration (i.e., low, medium) or for each Sample Delivery Group.³ Duplicates cannot be averaged for reporting on FORM I-IN.

Duplicate sample analyses are required for percent solids. Samples identified as field blanks cannot be used for duplicate sample analysis. EPA may require that a specific sample be used for duplicate sample analysis. If two analytical methods are used to obtain the reported values for the same element for a Sample Delivery Group (i.e., ICP, GFAA), duplicate samples must be run by each method used.

The relative percent differences (RPD) for each component are calculated as follows:

$$RPD = \frac{|S - D|}{(S+D)/2} \times 100$$

Where, RPD = Relative Percent Difference
S = First Sample Value (original)
D = Second Sample Value (duplicate)

The results of the duplicate sample analyses must be reported on FORM VI-IN in ug/L for aqueous samples and mg/Kg dry weight basis for solid original and duplicate samples. A control limit of 20% for RPD shall be used for original and duplicate sample values greater than or equal to 5x CRDL (Exhibit C). A control limit of (\pm) the CRDL must be used for sample values less than 5x CRDL, and the absolute value of the control limit (CRDL) must be entered in the "Control Limit" column on FORM VI-IN.

If one result is above the 5x CRDL level and the other is below, use the \pm CRDL criteria. If both sample values are less than the IDL, the RPD is not calculated on FORM VI-IN. For solid sample or duplicate results \leq 5x CRDL, enter the absolute value of the CRDL, corrected for sample weight and percent solids, in the "Control Limit" column.

If the duplicate sample results are outside the control limits, flag all the data for samples received associated with that duplicate sample with an "*" on FORMs I-IN and VI-IN. In the instance where there is more than one duplicate sample per SDG, if one duplicate result is not within contract criteria, flag all samples of the same matrix, concentration, and method in the SDG. The percent difference data will be used by EPA to evaluate the long-term precision of the methods for each parameter. Specific control limits for each element will be added to FORM VI-IN at a later date based on these precision results.

³EPA may require additional duplicate sample analyses, upon Project Officer request, for which the Contractor will be paid.

8. Laboratory Control Sample (LCS) Analysis

Aqueous and solid Laboratory Control Samples (LCS) must be analyzed for each analyte using the same sample preparations, analytical methods and QA/QC procedures employed for the EPA samples received. The aqueous LCS solution must be obtained from EPA (if unavailable, the Initial Calibration Verification Solutions may be used). One aqueous LCS must be prepared and analyzed for every group of aqueous samples in a Sample Delivery Group, or for each batch of aqueous samples digested, whichever is more frequent. An aqueous LCS is not required for mercury and cyanide analysis.

The EPA-provided solid LCS must be prepared and analyzed using each of the procedures applied to the solid samples received (exception: percent solids determination not required). If the EPA solid LCS is unavailable, other EPA Quality Assurance Check samples or other certified materials may be used. One solid LCS must be prepared and analyzed for every group of solid samples in a Sample Delivery Group, or for each batch of samples digested, whichever is more frequent.

All LCS results and percent recovery (%R) will be reported on FORM VII-IN. If the percent recovery for the aqueous LCS falls outside the control limits of 80-120% (exception: Ag and Sb), the analyses must be terminated, the problem corrected, and the samples associated with that LCS redigested and reanalyzed.

If the results for the solid LCS fall outside the control limits established by EPA, the analyses must be terminated, the problem corrected, and the samples associated with that LCS redigested and reanalyzed.

9. ICP Serial Dilution Analysis (L)

Prior to reporting concentration data for the analyte elements, the Contractor must analyze and report the results of the ICP Serial Dilution Analysis. The ICP Serial Dilution Analysis must be performed on a sample from each group of samples of a similar matrix type (i.e., water, soil) and concentration (i.e., low, medium) or for each Sample Delivery Group, whichever is more frequent. Samples identified as field blanks cannot be used for Serial Dilution Analysis.

If the analyte concentration is sufficiently high (minimally a factor of 50 above the instrumental detection limit in the original sample), the serial dilution (a five fold dilution) must then agree within 10% of the original determination after correction for dilution. If the dilution analysis for one or more analytes is not at or within 10%, a chemical or physical interference effect must be suspected, and the data for all affected analytes in the samples received associated with that serial dilution must be flagged with an "E" on FORM IX-IN and FORM I-IN.

The percent differences for each component are calculated as follows:

$$\% \text{ Difference} = \frac{|I - S|}{I} \times 100$$

where, I = Initial Sample Result

S = Serial Dilution Result (Instrument Reading x 5)

In the instance where there is more than one serial dilution per SDG, if one serial dilution result is not within contract criteria; flag all the samples of the same matrix and concentration in the Sample Delivery Group. Serial dilution results and "E" flags must be reported on FORM IX-IN.

10. Instrument Detection Limit (IDL) Determination

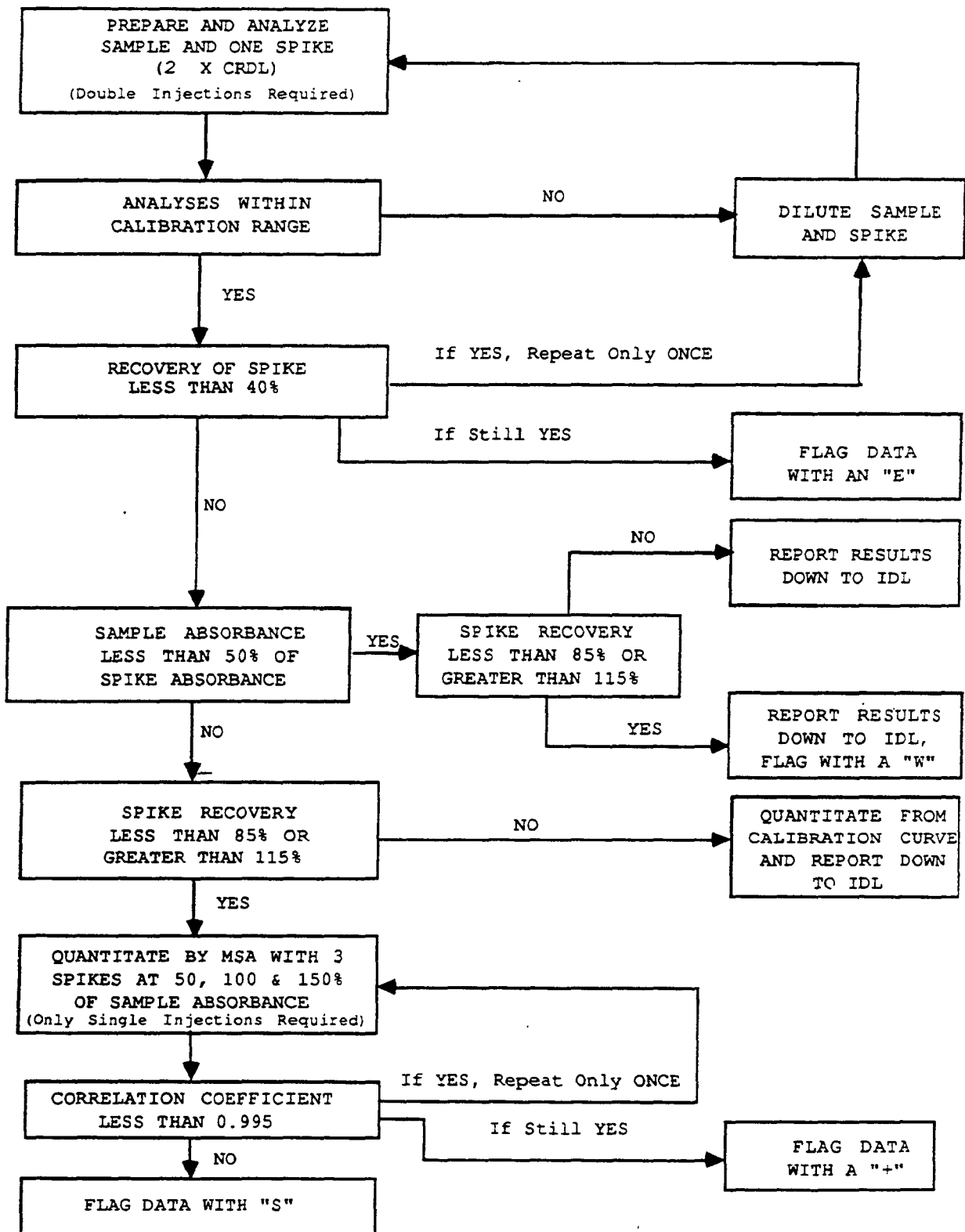
Before any field samples are analyzed under this contract, the instrument detection limits (in ug/L) must be determined for each instrument used, within 30 days of the start of contract analyses and at least quarterly (every 3 calendar months), and must meet the levels specified in Exhibit C.

The Instrument Detection Limits (in ug/L) shall be determined by multiplying by 3, the average of the standard deviations obtained on three nonconsecutive days from the analysis of a standard solution (each analyte in reagent water) at a concentration 3x-5x the instrument manufacturer's suggested IDL, with seven consecutive measurements per day. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDL's must be determined and reported for each wavelength used in the analysis of the samples.

The quarterly determined IDL for an instrument must always be used as the IDL for that instrument during that quarter. If the instrument is adjusted in anyway that may affect the IDL, the IDL for that instrument must be redetermined and the results submitted for use as the established IDL for that instrument for the remainder of the quarter.

IDLs must be reported for each instrument used on FORM X-IN submitted with each data package. If multiple AA instruments are used for the analysis of an element within a Sample Delivery Group, the highest IDL for the AAs must be used for reporting concentration values for that Sample Delivery Group. The same reporting procedure must be used for multiple ICPs.

Figure 1
FURNACE ATOMIC ABSORPTION ANALYSIS SCHEME



11. Interelement Corrections for ICP

Before any field samples are analyzed under this contract, the ICP interelement correction factors must be determined prior to the start of contract analyses and at least annually thereafter. Correction factors for spectral interference due to Al, Ca, Fe, and Mg must be determined for all ICP instruments at all wavelengths used for each analyte reported by ICP. Correction factors for spectral interference due to analytes other than Al, Ca, Fe, and Mg must be reported if they were applied.

If the instrument was adjusted in anyway that may affect the ICP interelement correction factors, the factors must be redetermined and the results submitted for use. Results from interelement correction factors determination must be reported on FORM XI(PART 1)-IN and FORM XI(PART 2)-IN for all ICP parameters.

12. Linear Range Analysis (LRA)

For all ICP analyses, a linear range verification check standard must be analyzed and reported quarterly (every 3 calendar months) for each element on FORM XII-IN. The standard must be analyzed during a routine analytical run performed under this contract. The analytically determined concentration of this standard must be within $\pm 5\%$ of the true value. This concentration is the upper limit of the ICP linear range beyond which results cannot be reported under this contract without dilution of the analytical sample.

13. Furnace Atomic Absorption (AA) QC Analyses

Because of the nature of the Furnace AA technique, the special procedures summarized in Figure 1-Furnace AA Analysis Scheme ("MSA Tree") will be required for quantitation. (These procedures do not replace those in Exhibit D of this SOW, but supplement the guidance provided therein.)

- a. All furnace analyses must fall within the calibration range. In addition, all analyses, except during full methods of Standard Addition (MSA), will require duplicate injections. The absorbance and concentration of each injection must be reported in the raw data as well as the average absorbance and concentration values. Average concentration values are used for reporting purposes. A maximum of 10 full sample analyses to a maximum 20 injections may be performed between each consecutive calibration verifications and blanks. The raw data package must contain absorbance and concentration values for both injections, the average value and the relative standard deviation (RSD) or coefficient of variation (CV). For concentrations greater than CRDL, the duplicate injection readings must agree within 20% RSD or CV, or the analytical sample must be rerun once (i.e., two additional burns). If the readings are still out, flag the value reported on FORM I-IN with an "M". The "M" flag is required for the analytical spike as well as the sample. If the analytical spike for a sample requires an "M" flag, the flag must be reported on FORM I-IN for that sample.

- b. All furnace analyses for each analytical sample, including those requiring an "M" flag, will require at least an analytical spike to determine if the MSA will be required for quantitation. The analytical spike⁴ will be required to be at a concentration (in the sample) 2x CRDL. This requirement for an analytical spike will include the LCS and the preparation blank. (The LCS must be quantitated from the calibration curve and corrective action, if needed, taken accordingly. MSA is not to be performed on the LCS or preparation blank, regardless of spike recovery results.) If the preparation blank analytical spike recovery is out of control (85-115%), the spiking solution must be verified by respiking and rerunning the preparation blank once. If the preparation blank analytical spike recovery is still out of control, correct the problem and reanalyze all analytical samples associated with that blank. An analytical spike is not required on the pre-digestion spike sample.

The analytical spike of a sample must be run immediately after that sample. The percent recovery (%R) of the spike, calculated by the same formula as Spike Sample Analyses (see item 6, this section), will then determine how the sample will be quantitated, as follows:

- 1) If the spike recovery is less than 40%, the sample must be diluted and rerun with another spike. Dilute the sample by a factor of 5 to 10 and rerun. This step must only be performed once. If after the dilution the spike recovery is still <40%, report data and flag with an "E" to indicate interference problems.
- 2) If the spike recovery is greater than or equal to 40% and the sample absorbance is less than 50% of the "spike"⁵, report the sample results to the IDL. If the spike recovery is less than 85% or greater than 115%, flag the result with a "W".
- 3) If the sample absorbance is greater than or equal to 50% of the spike and the spike recovery is at or between 85% and 115%, the sample must be quantitated directly from the calibration curve and reported down to the IDL.
- 4) If the sample absorbance is greater than or equal to 50% of the spike and the spike recovery is less than 85% or greater than 115%, the sample must be quantitated by MSA.

⁴Analytical Spikes are post-digestion spikes to be prepared prior to analysis by adding a known quantity of the analyte to an aliquot of the digested sample. The unspiked sample aliquot must be compensated for any volume change in the spike samples by addition of deionized water to the unspiked sample aliquot. The volume of the spiking solution added must not exceed 10% of the analytical sample volume; this requirement also applies to MSA spikes.

⁵"Spike" is defined as [absorbance of spike sample] minus [absorbance of the sample].

c. The following procedures will be incorporated into MSA analyses.

- 1) Data from MSA calculations must be within the linear range as determined by the calibration curve generated at the beginning of the analytical run.
- 2) The sample and three spikes must be analyzed consecutively for MSA quantitation (the "initial" spike run data is specifically excluded from use in the MSA quantitation). Only single injections are required for MSA quantitation.

Each full MSA counts as two analytical samples towards determining 10% QC frequency (i.e., five full MSAs can be performed between calibration verifications).

- 3) For analytical runs containing only MSAs, single injections can be used for QC samples during that run. For instruments that operate in an MSA mode only, MSA can be used to determine QC samples during that run.
- 4) Spikes must be prepared such that:
 - a) Spike 1 is approximately 50% of the sample absorbance.
 - b) Spike 2 is approximately 100% of the sample absorbance.
 - c) Spike 3 is approximately 150% of the sample absorbance.
- 5) The data for each MSA analysis must be clearly identified in the raw data documentation (using added concentration as the x-variable and absorbance as the y-variable) along with the slope, x-intercept, y-intercept and correlation coefficient (r) for the least squares fit of the data. The results must be reported on FORM VIII-IN. Reported values obtained by MSA must be flagged on the data sheet (FORM I-IN) with the letter "S" if the correlation coefficient is greater than or equal to 0.995.
- 6) If the correlation coefficient (r) for a particular analysis is less than 0.995, the MSA analysis must be repeated once. If the correlation coefficient is still less than 0.995, report the results on FORM I-IN from the run with the best "r" and flag the result with a "+" on FORM VIII-IN and FORM I-IN.

SECTION III
LABORATORY EVALUATION PROCESS

This document outlines the procedures which will be used by the Project Officer or his/her authorized representative to conduct laboratory audits to determine the Contractor's ability to meet the terms and conditions of this contract. The evaluation process incorporates two major steps: 1) evaluation of laboratory performance, and 2) on-site inspection of the laboratory to verify continuity of personnel, instrumentation and quality control requirements of the contract.

1. Evaluation of Laboratory Performance

a. Performance Evaluation Sample Analysis

- 1) The Performance Evaluation (PE) sample set will be sent to a participating laboratory on a quarterly basis to verify the laboratory's continuing ability to produce acceptable analytical results. These samples will be provided either single blind (recognizable as a PE material and of unknown composition), or double blind (not recognizable as PE material and of unknown composition). If received as a single blind, the Contractor is required to submit PE sample data in a separate SDG package in accordance with Delivery Schedule requirements for PE Sample data. PE samples received as double blind would be treated as routine samples and data would be submitted in the SDG deliverables package per normal procedure.
- 2) When the PE data are received by EPA, results will be scored routinely for identification and quantitation. Results of these scorings will be provided for the Contractor via coded evaluation spreadsheets by analyte. The Government may adjust the scores on any given PE sample to compensate for unanticipated difficulties with a particular sample.
- 3) If the Contractor laboratory performs unacceptably, the Contractor will be notified by the Project Officer. A laboratory so notified may expect, but the Government is not limited to, the following actions: a site visit, a full data audit, cessation of sample shipments, and/or laboratory analysis of a second PE sample. Failure by the laboratory to take corrective actions and/or failure of two successive PE sample analyses is indicative of Contractor failure to maintain technical competence and will require that the laboratory discontinue analysis of samples until such time as the Project Officer has determined that the laboratory has corrected the problem and may resume analyses.

b. Inorganic Data Audit

Inorganic data audits are conducted by EMSL-LV on the Contractor's sample data packages. The inorganic data audit provides the Agency with an in-depth inspection and evaluation of the data packages with regard to achieving QA/QC acceptability.

2. On-Site Laboratory Evaluation

The on-site laboratory evaluation helps to ensure that technical competence is maintained and that all the necessary quality control is being applied by the Contractor in order to deliver a quality product.

- a. On-site laboratory evaluations allow the evaluators to determine that:
 - 1) The organization and personnel are qualified to perform assigned tasks;
 - 2) Adequate facilities and equipment are available;
 - 3) Complete documentation, including chain-of-custody of samples is being implemented;
 - 4) Proper analytical methodology is being used;
 - 5) Adequate analytical quality control, including reference samples, control charts, and documented corrective action measures, is being provided; and
 - 6) Acceptable data handling and documentation techniques are being used.
- b. The on-site visit also serves as a mechanism for discussing weaknesses identified through Performance Evaluation sample analysis or through Contract Compliance Screening or other review of data deliverables. Lastly, the on-site visit allows the evaluation team to determine if the laboratory has implemented the recommended and/or required corrective actions, with respect to quality assurance, that were made during the previous on-site visit.

EXHIBIT F

CHAIN-OF-CUSTODY, DOCUMENT CONTROL,
AND STANDARD OPERATING PROCEDURES

1. Sample Chain-of-Custody

A sample is physical evidence collected from a facility or from the environment. An essential part of hazardous waste investigations is that samples and data may be used as evidence in EPA enforcement proceedings. To satisfy enforcement uses of the data, the following chain-of-custody procedures have been established.

1.1 Sample Identification

To ensure traceability of samples while in possession of the laboratory, a method for sample identification shall be developed and documented in laboratory Standard Operating Procedures (SOPs) (see Section 3). Each sample or sample preparation container shall be labeled with a unique number identifier (or the EPA Sample Number). This identifier shall be cross-referenced to the sample tag EPA Sample Number and the SMO number. There shall be a written description of the method of assigning this identifier and attaching it to the sample container included in the laboratory SOPs.

1.2.1 A sample is under custody if:

- 1.2.1.1 It is in your actual possession,
- 1.2.1.2 It is in your view after being in your physical possession,
- 1.2.1.3 It was in your possession and then you locked or sealed it up to prevent tampering, or
- 1.2.1.4 It is in a secure area.

1.2.2 Upon receipt of the samples in custody, the Contractor shall inspect the shipping container and sample bottles and shall document receiving information as specified in section 3.2. The sample custodian or a designated representative shall sign and date all appropriate receiving documents at the time of receipt (i.e., EPA chain-of-custody forms, Traffic Reports, airbills, etc.). The Contractor shall contact SMO if documents are absent, if information on receiving documents does not agree, if custody seals are not intact, or if the sample is not in good condition. The Contractor shall document resolution of any discrepancies, and this documentation shall become a part of the permanent Case file.

1.2.3 Once samples have been accepted by the laboratory, checked, and logged in, they must be maintained in accordance with custody and security requirements specified in 3.3.

2. Document Control Procedures

The goal of the laboratory document control program is to ensure that all documents for a specified Case will be accounted for when the project is completed. Accountable documents used by Contractor laboratories shall include, but not be limited to, logbooks, chain-of-custody records, sample work sheets, bench sheets, and other documents relating to the sample or sample analyses. The following document control procedures have been established to ensure that all laboratory records are assembled and stored for delivery to EPA or are available upon request from EPA prior to the delivery schedule.

2.1 Preprinted Data Sheets and Logbooks

Preprinted data sheets shall contain the name of the laboratory and be dated and signed by the analyst or individual performing the work. All documents produced by the laboratory which are directly related to the preparation and analysis of EPA samples shall become the property of the EPA and shall be placed in the Case file. For that reason, all observations and results recorded by the laboratory but not on preprinted data sheets shall be entered into permanent laboratory logbooks. The person responsible for the work shall sign and date each entry and/or page in the logbook. When all data from a case is compiled, copies of all EPA Case-related logbook entries shall be included in the documentation package. Analysts' logbook entries must be in chronological order and shall include only one Case per page. Instrument run logs shall be maintained so as to enable a reconstruction of the run sequences of individual instruments.

Because the laboratory must provide copies of the instrument run logs to EPA, the laboratory may exercise the option of using only laboratory or EPA sample identification numbers in the logs for sample ID rather than government agency or commercial client names.

Using laboratory or EPA Sample Number IDs only in the run sequences will assist the laboratory in preserving the confidentiality of commercial clients.

2.2 Error Correction Procedure

All documentation in logbooks and other documents shall be in ink. If an error is made, corrections shall be made by crossing a line through the error and entering the correct information. Changes shall be dated and initialed. No information shall be obliterated or rendered unreadable.

2.3 Consistency of Documentation

Before releasing analytical results, the laboratory shall assemble and cross-check the information on sample tags, custody records, lab bench sheets, personal and instrument logs, and other relevant data to ensure that data pertaining to each particular sample or Case is consistent throughout the Case file.

2.4 Document Numbering and Inventory Procedure

In order to provide document accountability of the completed analysis records, each item in a Case shall be inventoried and assigned a serialized number and identifier associating it to the Case and Region.

Case # - Region - Serialized number (For example: 75-2-0240)

The number of pages of each item must be accounted for if each page is not individually numbered. All documents relevant to each Case, including logbook pages, bench sheets, mass spectra, chromatograms, custody records, library search results, etc., shall be inventoried. The laboratory shall be responsible for ensuring that all documents generated are placed in the file for inventory and are delivered to EPA in the Case File Purge package (Exhibit B, Paragraph F). Figure 1 is an example of a document inventory.

2.5 Shipping Data Packages and Case Files

The Contractor shall have written procedures to document shipment of deliverables packages to the recipients. These shipments require custody seals on the containers placed such that it cannot be opened without damaging or breaking the seal. The Contractor shall also document what was sent, to whom, the date, and the method (carrier) used.

Figure 1

Example

232-2-0001
Case No. ____
Region ____

DOCUMENT INVENTORY

<u>Document Control #*</u>	<u>Document Type</u>	<u># Pages</u>
232-2-0001	Case File Document Inventory Sheet	1
232-2-0002	Chain-of-Custody Records	2
232-2-0003	Shipping Manifests	2
232-2-0004	Sample Tags	50
232-2-0005	SMO Inorganics Traffic Reports	10
232-2-0006	Inorganics Analysis Data Summary Sheets	10
232-2-0007	Analysts' Notebook Pages	14
232-2-0008	ICP and AA Instrument Logbook Pages	12
etc.	etc.	etc.

*This number is to be recorded on each set of documents.

3. Standard Operating Procedures

The Contractor must have written standard operating procedures (SOPs) for:

- a. Sample receipt and logging.
- b. Sample storage.
- c. Preventing sample contamination.
- d. Security for laboratory and samples.
- e. Traceability of standards.
- f. Maintaining instrument records and logbooks.
- g. Sample analysis and data control systems.
- h. Glassware cleaning.
- i. Technical and managerial review of laboratory operation and data package preparation.
- j. Internal review of contractually-required quality assurance and quality control data for each individual data package.
- k. Sample analysis, data handling and reporting.
- l. Chain-of-custody.
- m. Document control, including Case file preparation.

An SOP is defined as a written narrative step-by-step description of laboratory operating procedures including examples of laboratory documentation. The SOPs must accurately describe the actual procedures used in the laboratory, and copies of the written SOPs shall be available to the appropriate laboratory personnel. These procedures are necessary to ensure that analytical data produced under this contract are acceptable for use in EPA enforcement case preparation and litigation. The Contractor's SOPs shall provide mechanisms and documentation to meet each of the following specifications and shall be used by EPA as the basis for laboratory evidence audits.

- 3.1 The Contractor shall have a designated sample custodian responsible for receipt of samples and have written SOPs describing his/her duties and responsibilities.

- 3.2 The Contractor shall have written SOPs for receiving and logging in of the samples. The procedures shall include but not be limited to, documenting the following information:
- o Presence or absence of EPA chain-of-custody forms
 - o Presence or absence of airbills
 - o Presence or absence of EPA Traffic Reports or SAS packing lists
 - o Presence or absence of custody seals on shipping and/or sample containers and their condition
 - o Presence or absence of sample tags
 - o Sample tag ID numbers if not recorded on the chain-of-custody record(s) or packing list(s)
 - o Condition of the shipping container
 - o Condition of the sample bottles
 - o Verification of agreement or nonagreement of information on receiving documents
 - o Resolution of problems or discrepancies with the Sample Management Office
- 3.3 The Contractor shall have written SOPs for maintenance of the security of samples after log-in and shall demonstrate security of the sample storage and laboratory areas. The SOPs shall specifically include descriptions of all storage areas for EPA samples in the laboratory, and steps taken to prevent sample contamination. The SOPs shall include a list of authorized personnel who have access or keys to secure storage areas.
- 3.4 The Contractor shall have written SOPs for tracking the work performed on any particular sample. The tracking SOP shall include the following:
- 3.4.1 A description of the documentation used to record sample receipt, sample storage, sample transfers, sample preparations, and sample analyses.
 - 3.4.2 A description of the documentation used to record instrument calibration and other QA/QC activities.
 - 3.4.3 Examples of the document formats and laboratory documentation used in the sample receipt, sample storage, sample transfer, and sample analyses.

- 3.5 The Contractor shall have written SOPs for organization and assembly of all documents relating to each EPA Case, including technical and managerial review. Documents shall be filed on a Case-specific basis. The procedures must ensure that all documents including logbook pages, sample tracking records, chromatographic charts, computer printouts, raw data summaries, correspondence, and any other written documents having reference to the Case are compiled in one location for submission to EPA. The system must include a document numbering and inventory procedure.
- 3.6 The Contractor shall have written SOPs for laboratory safety.
- 3.7 The Contractor shall have written SOPs for cleaning of glassware used in preparing and analyzing samples under this contract.
- 3.8 The Contractor shall have SOPs for traceability of standards used in sample analysis QA/QC.

4. Handling of Confidential Information

A Contractor conducting work under this contract may receive EPA-designated confidential information from the Agency. Confidential information must be handled separately from other documentation developed under this contract. To accomplish this, the following procedures for the handling of confidential information have been established.

- 4.1 All confidential documents shall be under the supervision of a designated Document Control Officer (DCO).
- 4.2 Confidential Information

Any samples or information received with a request of confidentiality shall be handled as "confidential." A separate locked file shall be maintained to store this information and shall be segregated from other nonconfidential information. Data generated from confidential samples shall be treated as confidential. Upon receipt of confidential information, the DCO logs these documents into a Confidential Inventory Log. The information is then made available to authorized personnel but only after it has been signed out to that person by the DCO. The documents shall be returned to the locked file at the conclusion of each working day. Confidential information may not be reproduced except upon approval by the EPA Contracting Officer. The DCO will enter all copies into the document control system. In addition, this information may not be disposed of except upon approval by the EPA Contracting Officer. The DCO shall remove and retain the cover page of any confidential information disposed of for one year and shall keep a record of the disposition in the Confidential Inventory Log.

EXHIBIT G

GLOSSARY OF TERMS

GLOSSARY OF TERMS

ABSORBANCE - a measure of the decrease in incident light passing through a sample into the detector. It is defined mathematically as:

$$A = \frac{I(\text{solvent})}{I(\text{solution})} = \log \frac{I_0}{I}$$

Where, I - radiation intensity

ALIQOT - a measured portion of a field sample taken for analysis.

ANALYSIS DATE/TIME - the date and military time (24-hour clock) of the introduction of the sample, standard, or blank into the analysis system.

ANALYTE - the element or ion an analysis seeks to determine; the element of interest.

ANALYTICAL SAMPLE - Any solution or media introduced into an instrument on which an analysis is performed excluding instrument calibration, initial calibration verification, initial calibration blank, continuing calibration verification and continuing calibration blank. Note the following are all defined as analytical samples: undiluted and diluted samples (EPA and non-EPA), predigestion spike samples, duplicate samples, serial dilution samples, analytical spike samples, post-digestion spike samples, interference check samples (ICS), CRDL standard for AA (CRA), CRDL standard for ICP (CRI), laboratory control sample (LCS), preparation blank (PB) and linear range analysis sample (LRS).

ANALYTICAL SPIKE - The furnace post-digestion spike. The addition of a known amount of standard after digestion.

AUTOZERO - zeroing the instrument at the proper wavelength. It is equivalent to running a standard blank with the absorbance set at zero.

AVERAGE INTENSITY - The average of two different injections (exposures).

BACKGROUND CORRECTION - a technique to compensate for variable background contribution to the instrument signal in the determination of trace elements.

CALIBRATION - the establishment of an analytical curve based on the absorbance, emission intensity, or other measured characteristic of known standards. The calibration standards must be prepared using the same type of acid or concentration of acids as used in the sample preparation.

CALIBRATION BLANK - a volume of acidified deionized/distilled water.

CASE - a finite, usually predetermined number of samples collected over a given time period from a particular site. Case numbers are assigned by the Sample Management Office. A Case consists of one or more Sample Delivery Groups.

COEFFICIENT OF VARIATION (CV) - the standard deviation as a percent of the arithmetic mean.

CONCENTRATION LEVEL (low or medium) - for inorganics analysis, low or medium level is defined by the appropriate designation checked by the sampler on the Traffic Report.

CONTINUING CALIBRATION - analytical standard run every 10 analytical samples or every 2 hours, whichever is more frequent, to verify the calibration of the analytical system.

CONTRACT REQUIRED DETECTION LIMIT (CRDL) - minimum level of detection acceptable under the contract Statement of Work.

CONTROL LIMITS - a range within which specified measurement results must fall to be compliant. Control limits may be mandatory, requiring corrective action if exceeded, or advisory, requiring that noncompliant data be flagged.

CORRELATION COEFFICIENT - a number (r) which indicates the degree of dependence between two variables (concentration - absorbance). The more dependent they are the closer the value to one. Determined on the basis of the least squares line.

DAY - unless otherwise specified, day shall mean calendar day.

DIGESTION LOG - an official record of the sample preparation (digestion).

DISSOLVED METALS - analyte elements which have not been digested prior to analysis and which will pass through a 0.45 um filter.

DRY WEIGHT - the weight of a sample based on percent solids. The weight after drying in an oven.

DUPLICATE - a second aliquot of a sample that is treated the same as the original sample in order to determine the precision of the method.

FIELD BLANK - any sample submitted from the field identified as a blank.

FIELD SAMPLE - a portion of material received to be analyzed that is contained in single or multiple containers and identified by a unique EPA Sample Number.

FLAME ATOMIC ABSORPTION (AA) - atomic absorption which utilizes flame for excitation.

GRAPHITE FURNACE ATOMIC ABSORPTION (GFAA) - atomic absorption which utilizes a graphite cell for excitation.

HOLDING TIME - the elapsed time expressed in days from the date of receipt of the sample by the Contractor until the date of its analysis.

Holding time = (sample analysis date - sample receipt date)

INDEPENDENT STANDARD - a Contractor-prepared standard solution that is composed of analytes from a different source than those used in the standards for the initial calibration.

INDUCTIVELY COUPLED PLASMA (ICP) - a technique for the simultaneous or sequential multi-element determination of elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Characteristic atomic line emission spectra are produced by excitation of the sample in a radio frequency inductively coupled plasma.

IN-HOUSE - at the Contractor's facility.

INJECTION - introduction of the analytical sample into the instrument excitation system for the purpose of measuring absorbance, emission or concentration of an analyte. May also be referred to as exposure.

INSTRUMENT CALIBRATION - analysis of analytical standards for a series of different specified concentrations; used to define the quantitative response, linearity, and dynamic range of the instrument to target analytes.

INSTRUMENT DETECTION LIMIT (IDL) - determined by multiplying by three the standard deviation obtained for the analysis of a standard solution (each analyte in reagent water) at a concentration of 3x-5x IDL on three nonconsecutive days with seven consecutive measurements per day.

INTERFERENTS - substances which affect the analysis for the element of interest.

INTERNAL STANDARDS - in-house compounds added at a known concentration.

LABORATORY - synonymous with Contractor as used herein.

LABORATORY CONTROL SAMPLE (LCS) - a control sample of known composition. Aqueous and solid laboratory control samples are analyzed using the same sample preparation, reagents, and analytical methods employed for the EPA samples received.

LABORATORY RECEIPT DATE - the date on which a sample is received at the Contractor's facility, as recorded on the shipper's delivery receipt and sample Traffic Report. Also referred to as VTSR (validated time of sample receipt).

LINEAR RANGE, LINEAR DYNAMIC RANGE - the concentration range over which the ICP analytical curve remains linear.

MATRIX - the predominant material of which the sample to be analyzed is composed. For the purpose of this SOW, a sample matrix is either water or soil/sediment. Matrix is not synonymous with phase (liquid or solid).

MATRIX MODIFIER - salts used in AA to lessen the effects of chemical interferents, viscosity, and surface tension.

MATRIX SPIKE - aliquot of a sample (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

METHOD OF STANDARD ADDITIONS (MSA) - the addition of 3 increments of a standard solution (spikes) to sample aliquots of the same size. Measurements are made on the original and after each addition. The slope, x-intercept and y-intercept are determined by least-square analysis. The analyte concentration is determined by the absolute value of the x-intercept. Ideally, the spike volume is low relative to the sample volume (approximately 10% of the volume). Standard addition may counteract matrix effects; it will not counteract spectral effects. Also referred to as Standard Addition.

PERCENT SOLIDS - the proportion of solid in a soil sample determined by drying an aliquot of the sample.

PERFORMANCE EVALUATION (PE) SAMPLE - a sample of known composition provided by EPA for Contractor analysis. Used by EPA to evaluate Contractor performance.

PREPARATION BLANK (reagent blank, method blank) - an analytical control that contains distilled, deionized water and reagents, which is carried through the entire analytical procedure (digested and analyzed). An aqueous method blank is treated with the same reagents as a sample with a water matrix; A solid method blank is treated with the same reagents as a soil sample.

PROTOCOL - a compilation of the procedures to be followed with respect to sample receipt and handling, analytical methods, data reporting and deliverables, and document control. Used synonymously with Statement of Work (SOW).

ROUNDING RULES - If the figure following those to be retained is less than 5, the figure is dropped, and the retained figures are kept unchanged. As an example, 11.443 is rounded off to 11.44.

If the figure following those to be retained is greater than 5, the figure is dropped, and the last retained figure is raised by 1. As an example, 11.446 is rounded off to 11.45.

If the figure following those to be retained is 5, and if there are no figures other than zeros beyond the five, the figure 5 is dropped, and the last-place figure retained is increased by one if it is an odd number or it is kept unchanged if an even number. As an example, 11.435 is rounded off to 11.44, while 11.425 is rounded off to 11.42.

If a series of multiple operations is to be performed (add, subtract, divide, multiply), all figures are carried through the calculations. Then the final answer is rounded to the proper number of significant figures.

See forms instructions (Exhibit B) for exceptions.

RUN - a continuous analytical sequence consisting of prepared samples and all associated quality assurance measurements as required by the contract Statement of Work.

SAMPLE DELIVERY GROUP (SDG) - a unit within a sample Case that is used to identify a group of samples for delivery. An SDG is a group of 20 or fewer samples within a Case, received over a period of up to 14 calendar days. Data from all samples in an SDG are due concurrently. A Sample Delivery Group is defined by one of the following, whichever occurs first:

- o Case; or
- o Each 20 samples within a Case; or
- o Each 14-day calendar period during which samples in a Case are received, beginning with receipt of the first sample in the Case or SDG.

Samples may be assigned to Sample Delivery Groups by matrix (i.e., all soils in one SDG, all waters in another), at the discretion of the laboratory.

SAMPLE NUMBER (EPA SAMPLE NUMBER) - a unique identification number designated by EPA for each sample. The EPA Sample Number appears on the sample Traffic Report which documents information on that sample.

SERIAL DILUTION - the dilution of a sample by a factor of five. When corrected by the dilution factor, the diluted sample must agree with the original undiluted sample within specified limits. Serial dilution may reflect the influence of interferents.

SOIL - synonymous with soil/sediment or sediment as used herein.

STOCK SOLUTION - a standard solution which can be diluted to derive other standards.

TOTAL METALS - analyte elements which have been digested prior to analysis.

TRAFFIC REPORT (TR) - an EPA sample identification form filled out by the sampler, which accompanies the sample during shipment to the laboratory and which is used for documenting sample condition and receipt by the laboratory.

WET WEIGHT - the weight of a sample aliquot including moisture (undried).

10% FREQUENCY - a frequency specification during an analytical sequence allowing for no more than 10 analytical samples between required calibration verification measurements, as specified by the contract Statement of Work.

EXHIBIT H

DATA DICTIONARY AND FORMAT FOR DATA DELIVERABLES
IN COMPUTER-READABLE FORMAT

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SECTION II: Format A Specification	H-3
SECTION III: Format B Specification	H-26

SECTION I
DESCRIPTION OF DELIVERABLES

1. Introduction

- 1.1 Two file formats are specified for delivery of computer-readable data. Format A is oriented to the structure of the hardcopy reporting forms required by the contract. Format B is oriented to the general data required by the contract. Information sufficient to generate required hardcopy forms is contained in either format.
- 1.2 The file or files for a Sample Delivery Group (SDG, see Exhibit A, Section I, B) must be submitted on a diskette or diskettes (see paragraph, 2.1). Information on a diskette or diskettes for any single SDG must be in one, and only one, of the two formats. The format used is at the option of the laboratory. The option used must be included in the File Name specification (paragraph 2.2).
- 1.3 Format A consists of variable length ASCII records, and Format B consists of fixed-length 80-byte ASCII records.
- 1.4 All information for one SDG must be in one file if format A is used. Use of Format B may require information for one SDG to be in a number of files. Format B may require more than one 360 K diskette for a valid SDG.

2. Deliverable

- 2.1 The file or files must be submitted on a 5-1/4 inch floppy diskette, which may be either a double-sided, double density, 360 K-byte or a high capacity 1.2 M-byte diskette. The diskette must be formatted and recorded using the MS-DOS Operating System. The diskette or diskettes must contain all information relevant to one and only one SDG, and must accompany the hardcopy package for the SDG submitted to the Sample Management Office (see Exhibit B). Information on the diskette or diskettes must correspond exactly with information submitted in the hardcopy data package and on the hardcopy data package forms. Blank or unused records in either format should not be included on the diskettes.
- 2.2 Each diskette must be identified with an external label containing (in this order) the following information:

Disk Density
File Name(s)
Laboratory Name (optional)
Laboratory Code
Case Number (where applicable)
SAS Number (where applicable)

The format for the File Name(s) must be XXXXXX.INY

where XXXXXX is the SDG identifier

- I indicates Inorganics analysis
- N is a continuation number used to identify multiple files corresponding to the same SDG. For Format A, "N" must be "1". For Format B, "N" must be "1" for the only, or first file of the SDG, and must be incremented to "2", "3", etc., for subsequent files of the SDG. "N" cannot be greater than 9
- Y is "A" for Format A or "B" for Format B

Dimensions of the label must be in the range 4-3/4" to 5" long by 1-1/4" to 1-1/2" wide.

SECTION II
FORMAT A SPECIFICATION

1. Format Characteristics

- 1.1 Format A is based upon the structure of the hardcopy reporting forms required by the contract. With two exceptions, Form Suffix and Record Type, all fields in the format correspond directly with entries or items on the hardcopy forms.
- 1.2 Format A includes detailed specifications for the required format of each Inorganic Reporting Form's HEADER and DETAIL records. The exact columns in which each field is to be contained are shown, as well as the length of the field. Each field's required contents are specified either as a literal (contained in single quotes) which must appear exactly as shown (without the quotes), or as a variable for which a format is listed in the format column. Each field's required format is specified either as an option of two or more choices (divided by slashes), as MM/DD/YY for a date, as a CHARACTER field, or as a NUMERIC field.
- 1.3 Format fields listed as CHARACTER may contain any standard ASCII characters, and must be left-justified and padded with blanks. Formats listed as NUMERIC may contain numeric digits, a decimal point, and a leading plus or minus sign, and must be right-justified and padded with blanks. The numbers following the word NUMERIC specify the maximum number of digits which are allowed on either side of the decimal. The decimal point is not assumed and must be contained in the field in its correct position. For example, the format "NUMERIC 3.2" allows 3 digits preceding the decimal point and 2 following it (a total length of 6 characters). The format "NUMERIC S3.2" allows a leading plus or minus sign (a total length of 7). If a field's format description does not contain a decimal point, then a decimal point is not allowed in the field. If a field's format description does not contain an "S", then a sign is not allowed in the field.

Explanation of NUMERIC fields in Format A.

In the examples below the format NUMERIC 3.2 is described.

(Quotation marks indicate limits of the field described and are not included in the format.)

If the value of the field is 10.1:

The columns in the format will appear as: "10.10" (six columns).

The table below demonstrates several examples:

Value	Appears on Format
10.1	"10.10"
10.11	"10.11"
100.11	"100.11"
100	"100.00"
.29	"0.29"
-100.129	Invalid
-10.1	Invalid

The following table presents examples of NUMERIC S3.2:

Value	Appears on Format
10.1	" 10.10" (seven columns)
-10.11	" -10.11"
-100.11	" -100.11"
-1000.1	Invalid
100	" 100.00"
-.22	" -0.22"
-.239	" -0.24"

2. Record Types

- 2.1 Format A consists of variable length ASCII records. The last two bytes of each record must contain "carriage return" and "line feed", respectively. Unused bytes in partially filled fields must be blank-filled.
- 2.2 Format A has three types of records: Header Records, Detail Records and Comment Records.

<u>Type</u>	<u>Type ID</u>	<u>Contents</u>
Header	H	Nonrepeating fields which together are unique to the associated hardcopy form
Detail	D	A group of fields that are repeated on a form, and are uniquely positioned by (e.g., Analyte Chemical Symbol)
Comment	C	Nonrepeating fields containing text that comments on information reported on the form

The format for Comment Records is the same for all forms, and is described after all other formats.

- 2.3 The first 5 bytes of each record contain the FORM ID, identifying the Inorganic Analysis Reporting Form for which the record contains data. The ID must be left-justified in the field.

<u>FORM ID</u>	<u>FORM NAME</u>
COVER	COVER PAGE - INORGANIC ANALYSES DATA PACKAGE
I	INORGANIC ANALYSIS DATA SHEET
II(1)	INITIAL AND CONTINUING CALIBRATION VERIFICATION
II(2)	CRDL STANDARD FOR AA AND ICP
III	BLANKS
IV	ICP INTERFERENCE CHECK SAMPLE
V(1)	SPIKE SAMPLE RECOVERY
V(2)	POST DIGEST SPIKE SAMPLE RECOVERY
VI	DUPLICATES
VII	LABORATORY CONTROL SAMPLE
VIII	STANDARD ADDITION RESULTS
IX	ICP SERIAL DILUTIONS
X	INSTRUMENT DETECTION LIMITS (QUARTERLY)
XI	ICP INTERELEMENT CORRECTION FACTORS (ANNUALLY)
XII	ICP LINEAR RANGES (QUARTERLY)
XIII	PREPARATION LOG
XIV	ANALYSIS RUN LOG

Following the FORM ID is a two-byte, left-justified, FORM SUFFIX, which must be unique for each set of records that correspond to one hardcopy form. For example, records for the first occurrence of a form must contain the suffix AA. Records for the second occurrence must contain AB, and the twenty-seventh occurrence would contain BA.

The 8th byte of each record contains the TYPE ID, which specifies what kind of data the record contains (see paragraph 2.2).

Records with the same FORM ID and FORM SUFFIX must be grouped together in the file. Within each FORM ID/FORM SUFFIX group, there may be only one HEADER record, and it must come first. DETAIL records must follow the HEADER record. The COMMENT records, which are optional, must come last in the group, and be in sequence corresponding to the form.

The FORM ID/FORM SUFFIX group(s) for the COVER PAGE(S) must come first in the file. After the COVER PAGE(S), the FORM ID/FORM SUFFIX groups do not have to be in any specific order. For example, a set of HEADER/DETAIL/COMMENT records for FORM V could come before records for FORM I, as long as the records within the group are in the correct order.

3. Record Length

Table 3.1 summarizes the length (excluding carriage return/line feed) and (in parentheses) the number of records in Format A. The maximum number of detail and comment records is shown, corresponding to a submission of hardcopy forms on which information is written on all possible lines.

Table 3.1 Format A Summary

<u>Form</u>	<u>Record</u>		
	<u>Header</u>	<u>Detail</u>	<u>Comment</u>
Cover	80 ^a (1) ^b	25(24)	78(4)
I	90(1)	31(24)	78(4)
II(1)	32(1)	65(24)	
II(2)	32(1)	66(23)	
III	18(1)	59(24)	
IV	32(1)	64(23)	
V(1)	33(1)	66(24)	78(4)
V(2)	23(1)	62(24)	78(4)
VI	38(1)	56(24)	
VII	32(1)	68(24)	
VIII	8(1)	67(32)	
IX	23(1)	44(23)	
X	52(1)	29(23)	78(4)
XI	28(1)	77(23)	78(4)
XII	28(1)	29(23)	78(4)
XIII	10(1)	32(32)	
XIV	38(1)	59(32)	

^a Length of record in bytes (excluding carriage return/line feed).

^b Maximum number of records required for a form.

4. Record Listing

The remainder of this section contains detailed specifications for every record required for a full set of hardcopy forms.

COVER PAGE

INORGANIC ANALYSES DATA PACKAGE COVER PAGE HEADER RECORD:

<u>COLUMN(S)</u>	<u>LENGTH</u>	<u>CONTENTS</u>	<u>FORMAT</u>
1-5	5	'COVER'	
6-7	2	FORM SUFFIX	
8	1	'H'	
9-33	25	LAB NAME	CHARACTER
34-43	10	CONTRACT	CHARACTER
44-49	6	LAB CODE	CHARACTER
50-54	5	CASE NUMBER	CHARACTER
55-60	6	SAS NUMBER	CHARACTER
61-66	6	SDG NUMBER	CHARACTER
67-71	5	SOW NUMBER	CHARACTER
72-74	3	ICP INT CORRECTIONS	'YES'/'NO'
75-77	3	ICP BG CORRECTIONS	'YES'/'NO'
78-80	3	RAW DATA BEFORE	'YES'/'NO'/BLANK

NOTE: The LAB NAME, CONTRACT, LAB CODE, CASE NUMBER, SAS NUMBER, AND SDG NUMBER, which are contained in the COVER PAGE HEADER record, are not repeated in the HEADER records of the other forms. Each form's HEADER record contains only data which are unique to the DETAIL records which follow it.

INORGANIC ANALYSES DATA PACKAGE COVER PAGE DETAIL RECORDS:

<u>COLUMN(S)</u>	<u>LENGTH</u>	<u>CONTENTS</u>	<u>FORMAT</u>
1-5	5	'COVER'	
6-7	2	FORM SUFFIX	
8	1	'D'	
9-15	7	EPA SAMPLE NO.	CHARACTER
16-25	10	LAB SAMPLE ID NO.	CHARACTER

FORM I

INORGANIC ANALYSIS DATA SHEET HEADER RECORD:

<u>COLUMN(S)</u>	<u>LENGTH</u>	<u>CONTENTS</u>	<u>FORMAT</u>
1-5	5	'I '	
6-7	2	FORM SUFFIX	
8	1	'H'	
9-15	7	EPA SAMPLE NO.	CHARACTER
16-20	5	MATRIX	'WATER'/'SOIL'
21-30	10	LAB SAMPLE ID	CHARACTER
31-33	3	LEVEL	'LOW'/'MED'
34-41	8	DATE RECEIVED	MM/DD/YY
42-46	5	PERCENT SOLIDS	NUMERIC 3.1
47-51	5	CONCENTRATION UNITS	'UG/L'/'MG/KG'
52-60	9	COLOR BEFORE	CHARACTER
61-69	9	COLOR AFTER	CHARACTER
70-75	6	CLARITY BEFORE	CHARACTER
76-81	6	CLARITY AFTER	CHARACTER
82-87	6	TEXTURE	CHARACTER
88-90	3	ARTIFACTS	'YES'/BLANK

INORGANIC ANALYSIS DATA SHEET DETAIL RECORDS:

<u>COLUMN(S)</u>	<u>LENGTH</u>	<u>CONTENTS</u>	<u>FORMAT</u>
1-5	5	'I '	
6-7	2	FORM SUFFIX	
8	1	'D'	
9-10	2	ANALYTE SYMBOL	CHARACTER
11-22	12	CONCENTRATION	NUMERIC 9.2
23	1	CONC FLAG (C)	'B'/'U'/BLANK
24-29	6	QUALIFIER (Q)	UP TO 6 ONE-CHARACTER FLAGS (OTHER THAN 'B' OR 'U')
30-31	2	METHOD (M)	METHOD CODE/'NR'

FORM II (PART 1)

INITIAL AND CONTINUING CALIBRATION VERIFICATION HEADER RECORD:

<u>COLUMN(S)</u>	<u>LENGTH</u>	<u>CONTENTS</u>	<u>FORMAT</u>
1-5	5	'II(1)'	
6-7	2	FORM SUFFIX	
8	1	'H'	
9-20	12	INIT CAL SOURCE	CHARACTER
21-32	12	CONT CAL SOURCE	CHARACTER

INITIAL AND CONTINUING CALIBRATION VERIFICATION DETAIL RECORDS:

<u>COLUMN(S)</u>	<u>LENGTH</u>	<u>CONTENTS</u>	<u>FORMAT</u>
1-5	5	'II(1)'	
6-7	2	FORM SUFFIX	
8	1	'D'	
9-10	2	ANALYTE SYMBOL	CHARACTER
11-17	7	INITIAL CAL TRUE	NUMERIC 5.1
18-25	8	INITIAL CAL FOUND	NUMERIC 5.2
26-30	5	INITIAL CAL %R	NUMERIC 3.1
31-37	7	CONT CAL TRUE	NUMERIC 5.1
38-45	8	CONT CAL FOUND 1	NUMERIC 5.2
46-50	5	CONT CAL %R 1	NUMERIC 3.1
51-58	8	CONT CAL FOUND 2	NUMERIC 5.2
59-63	5	CONT CAL %R 2	NUMERIC 3.1
64-65	2	METHOD (M)	METHOD CODE/'NR'

FORM II (PART 2)

CRDL STANDARD FOR AA AND ICP HEADER RECORD:

<u>COLUMN(S)</u>	<u>LENGTH</u>	<u>CONTENTS</u>	<u>FORMAT</u>
1-5	5	'II(2)'	
6-7	2	FORM SUFFIX	
8	1	'H'	
9-20	12	AA STANDARD SOURCE	CHARACTER
21-32	12	ICP STANDARD SOURCE	CHARACTER

CRDL STANDARD FOR AA AND ICP DETAIL RECORDS:

<u>COLUMN(S)</u>	<u>LENGTH</u>	<u>CONTENTS</u>	<u>FORMAT</u>
1-5	5	'II(2)'	
6-7	2	FORM SUFFIX	
8	1	'D'	
9-10	2	ANALYTE SYMBOL	CHARACTER
11-17	7	AA TRUE	NUMERIC 5.1
18-26	9	AA FOUND	NUMERIC 6.2
27-31	5	AA %R	NUMERIC 3.1
32-38	7	ICP INIT TRUE	NUMERIC 5.1
39-47	9	ICP INIT FOUND	NUMERIC 6.2
48-52	5	ICP INIT %R	NUMERIC 3.1
53-61	9	ICP FINAL FOUND	NUMERIC 6.2
62-66	5	ICP FINAL %R	NUMERIC 3.1

FORM III

BLANKS HEADER RECORD:

<u>COLUMN(S)</u>	<u>LENGTH</u>	<u>CONTENTS</u>	<u>FORMAT</u>
1-5	5	'III '	
6-7	2	FORM SUFFIX	
8	1	'H'	
9-13	5	PREP BLANK MATRIX	'WATER'/'SOIL '
14-18	5	PREP BLANK UNITS	'UG/L '/'MG/KG'

BLANKS DETAIL RECORDS:

<u>COLUMN(S)</u>	<u>LENGTH</u>	<u>CONTENTS</u>	<u>FORMAT</u>
1-5	5	'III '	
6-7	2	FORM SUFFIX	
8	1	'D'	
9-10	2	ANALYTE SYMBOL	CHARACTER
11-18	8	INITIAL CAL BLANK	NUMERIC S5.1
19	1	INITIAL CAL FLAG (C)	'B'/'U'/BLANK
20-27	8	CONT CAL BLANK 1	NUMERIC S5.1
28	1	CC BLANK 1 FLAG (C)	'B'/'U'/BLANK
29-36	8	CONT CAL BLANK 2	NUMERIC S5.1
37	1	CC BLANK 2 FLAG (C)	'B'/'U'/BLANK
38-45	8	CONT CAL BLANK 3	NUMERIC S5.1
46	1	CC BLANK 3 FLAG (C)	'B'/'U'/BLANK
47-56	10	PREPARATION BLANK	NUMERIC S5.3
57	1	PREP BLANK FLAG (C)	'B'/'U'/BLANK
58-59	2	METHOD (M)	METHOD CODE/'NR'

FORM IV

ICP INTERFERENCE CHECK SAMPLE HEADER RECORD:

<u>COLUMN(S)</u>	<u>LENGTH</u>	<u>CONTENTS</u>	<u>FORMAT</u>
1-5	5	'IV	
6-7	2	FORM SUFFIX	
8	1	'H'	
9-20	12	ICP ID NUMBER	CHARACTER
19-32	12	ICS SOURCE	CHARACTER

ICP INTERFERENCE CHECK SAMPLE DETAIL RECORDS:

<u>COLUMN(S)</u>	<u>LENGTH</u>	<u>CONTENTS</u>	<u>FORMAT</u>
1-5	5	'IV '	
6-7	2	FORM SUFFIX	
8	1	'D'	
9-10	2	ANALYTE SYMBOL	CHARACTER
11-16	6	TRUE A	NUMERIC 6
17-22	6	TRUE AB	NUMERIC 6
23-29	7	INITIAL A	NUMERIC S6
30-38	9	INITIAL AB	NUMERIC S6.1
39-43	5	INITIAL %R	NUMERIC 3.1
44-50	7	FINAL A	NUMERIC S6
51-59	9	FINAL AB	NUMERIC S6.1
60-64	5	FINAL %R	NUMERIC 3.1

FORM V (PART 1)

SPIKE SAMPLE RECOVERY HEADER RECORD:

<u>COLUMN(S)</u>	<u>LENGTH</u>	<u>CONTENTS</u>	<u>FORMAT</u>
1-5	5	'V(1) '	
6-7	2	FORM SUFFIX	
8	1	'H'	
9-15	7	EPA SAMPLE NO.	CHARACTER
16-20	5	MATRIX	'WATER'/'SOIL '
21-23	3	LEVEL	'LOW'/'MED'
24-28	5	CONCENTRATION UNITS	'UG/L ' / 'MG/KG'
29-33	5	SAMPLE & SOLIDS	NUMERIC 3.1

SPIKE SAMPLE RECOVERY DETAIL RECORDS:

<u>COLUMN(S)</u>	<u>LENGTH</u>	<u>CONTENTS</u>	<u>FORMAT</u>
1-5	5	'V(1) '	
6-7	2	FORM SUFFIX	
8	1	'D'	
9-10	2	ANALYTE SYMBOL	CHARACTER
11-16	6	CONTROL LIMIT %R	'75-125'/BLANK
17-30	14	SPIKED SAMPLE RESULT	NUMERIC 9.4
31	1	SSR FLAG (C)	'B'/'U'/BLANK
32-44	13	SAMPLE RESULT	NUMERIC 8.4
45	1	SR FLAG (C)	'B'/'U'/BLANK
46-56	11	SPIKE ADDED	NUMERIC 8.2
57-63	7	PERCENT RECOVERED	NUMERIC S4.1
64	1	QUALIFIER (Q)	'N'/BLANK
65-66	2	METHOD (M)	METHOD CODE/'NR'

FORM V (PART 2)

POST DIGEST SPIKE SAMPLE RECOVERY HEADER RECORD:

<u>COLUMN(S)</u>	<u>LENGTH</u>	<u>CONTENTS</u>	<u>FORMAT</u>
1-5	5	'V(2) '	
6-7	2	FORM SUFFIX	
8	1	'H'	
9-15	7	EPA SAMPLE NO.	CHARACTER
16-20	5	MATRIX	'WATER'/'SOIL '
21-23	3	LEVEL	'LOW'/'MED'

POST DIGEST SPIKE SAMPLE RECOVERY DETAIL RECORDS:

<u>COLUMN(S)</u>	<u>LENGTH</u>	<u>CONTENTS</u>	<u>FORMAT</u>
1-5	5	'V(2) '	
6-7	2	FORM SUFFIX	
8	1	'D'	
9-10	2	ANALYTE SYMBOL	CHARACTER
11-16	6	CONTROL LIMIT %R	BLANK
17-28	12	SPIKED SAMPLE RESULT	NUMERIC 9.2
29	1	SSR FLAG.(C)	'B'/'U'/BLANK
30-41	12	SAMPLE RESULT	NUMERIC 9.2
42	1	SR FLAG (C)	'B'/'U'/BLANK
43-52	10	SPIKE ADDED	NUMERIC 8.1
53-59	7	PERCENT RECOVERED	NUMERIC S4.1
60	1	QUALIFIER (Q)	BLANK
61-62	2	METHOD (M)	METHOD CODE/'NR'

FORM VI

DUPLICATES HEADER RECORD:

<u>COLUMN(S)</u>	<u>LENGTH</u>	<u>CONTENTS</u>	<u>FORMAT</u>
1-5	5	'VI '	
6-7	2	FORM SUFFIX	
8	1	'H'	
9-15	7	EPA SAMPLE NO.	CHARACTER
16-20	5	MATRIX	'WATER'/'SOIL '
21-23	3	LEVEL	'LOW'/'MED'
24-28	5	CONCENTRATION UNITS	'UG/L '/'MG/KG'
29-33	5	SAMPLE & SOLIDS	NUMERIC 3.1
34-38	5	DUPLICATE & SOLIDS	NUMERIC 3.1

DUPLICATES DETAIL RECORDS:

<u>COLUMN(S)</u>	<u>LENGTH</u>	<u>CONTENTS</u>	<u>FORMAT</u>
1-5	5	'VI '	
6-7	2	FORM SUFFIX	
8	1	'D'	
9-10	2	ANALYTE SYMBOL	CHARACTER
11-17	7	CONTROL LIMIT	NUMERIC 5.1
18-31	14	SAMPLE	NUMERIC 9.4
32	1	SAMPLE FLAG (C)	'B'/'U'/BLANK
33-46	14	DUPLICATE	NUMERIC 9.4
47	1	DUPLICATE FLAG (C)	'B'/'U'/BLANK
48-53	6	RPD	NUMERIC 4.1
54	1	QUALIFIER (Q)	'*'/BLANK
55-56	2	METHOD (M)	METHOD CODE/'NR'

FORM VII

LABORATORY CONTROL SAMPLE HEADER RECORD:

<u>COLUMN(S)</u>	<u>LENGTH</u>	<u>CONTENTS</u>	<u>FORMAT</u>
1-5	5	'VII '	
6-7	2	FORM SUFFIX	
8	1	'H'	
9-20	12	SOLID LCS SOURCE	CHARACTER
21-32	12	AQUEOUS LCS SOURCE	CHARACTER

LABORATORY CONTROL SAMPLE DETAIL RECORDS:

<u>COLUMN(S)</u>	<u>LENGTH</u>	<u>CONTENTS</u>	<u>FORMAT</u>
1-5	5	'VII '	
6-7	2	FORM SUFFIX	
8	1	'D'	
9-10	2	ANALYTE SYMBOL	CHARACTER
11-17	7	AQUEOUS TRUE	NUMERIC 5.1
18-25	8	AQUEOUS FOUND	NUMERIC 5.2
26-30	5	AQUEOUS % RECOVERED	NUMERIC 3.1
31-38	8	SOLID TRUE	NUMERIC 6.1
39-46	8	SOLID FOUND	NUMERIC 6.1
47	1	SOLID FOUND FLAG (C)	'B'/'U'/BLANK
48-55	8	SOLID LOWER LIMIT	NUMERIC 6.1
56-63	8	SOLID UPPER LIMIT	NUMERIC 6.1
64-68	5	SOLID % RECOVERED	NUMERIC 3.1

FORM VIII

STANDARD ADDITION RESULTS HEADER RECORD:

<u>COLUMN(S)</u>	<u>LENGTH</u>	<u>CONTENTS</u>	<u>FORMAT</u>
1-5	5	'VIII '	
6-7	2	FORM SUFFIX	
8	1	'H'	

NOTE: Although there are no fields which occur only once per FORM VIII, the HEADER record must be included as a place holder, indicating that DETAIL records follow.

STANDARD ADDITION RESULTS DETAIL RECORDS:

<u>COLUMN(S)</u>	<u>LENGTH</u>	<u>CONTENTS</u>	<u>FORMAT</u>
1-5	5	'VIII '	
6-7	2	FORM SUFFIX	
8	1	'D'	
9-15	7	EPA SAMPLE NO.	CHARACTER
16-17	2	ANALYTE SYMBOL	CHARACTER
18-24	7	0 ADD ABSORBANCE	NUMERIC 3.3
25-26	2	1 ADD CONCENTRATION	NUMERIC 2
27-33	7	1 ADD ABSORBANCE	NUMERIC 3.3
34-36	3	2 ADD CONCENTRATION	NUMERIC 3
37-43	7	2 ADD ABSORBANCE	NUMERIC 3.3
44-46	3	3 ADD CONCENTRATION	NUMERIC 3
47-53	7	3 ADD ABSORBANCE	NUMERIC 3.3
54-60	7	FINAL CONCENTRATION	NUMERIC 5.1
61-66	6	CORRELATION COEF (R)	NUMERIC 1.4
67	1	QUALIFIER (Q)	'+' / BLANK

FORM IX

ICP SERIAL DILUTIONS HEADER RECORD:

<u>COLUMN(S)</u>	<u>LENGTH</u>	<u>CONTENTS</u>	<u>FORMAT</u>
1-5	5	'IX '	
6-7	2	FORM SUFFIX	
8	1	'H'	
9-15	7	EPA SAMPLE NO.	CHARACTER
16-20	5	MATRIX	'WATER'/'SOIL
21-23	3	LEVEL	'LOW'/'MED'

ICP SERIAL DILUTIONS DETAIL RECORDS:

<u>COLUMN(S)</u>	<u>LENGTH</u>	<u>CONTENTS</u>	<u>FORMAT</u>
1-5	5	'IX '	
6-7	2	FORM SUFFIX	
8	1	'D'	
9-10	2	ANALYTE SYMBOL	CHARACTER
11-22	12	INIT SAMPLE (I)	NUMERIC 9.2
23	1	INIT SAMPLE FLAG (C)	'B'/'U'/BLANK
24-35	12	SERIAL DILUTION (S)	NUMERIC 9.2
36	1	DILUTION FLAG (C)	'B'/'U'/BLANK
37-41	5	PERCENT DIFFERENCE	NUMERIC 3.1
42	1	QUALIFIER (Q)	'E'/BLANK
43-44	2	METHOD (M)	METHOD CODE/'NR'

FORM X

INSTRUMENT DETECTION LIMITS (QUARTERLY) HEADER RECORD:

<u>COLUMN(S)</u>	<u>LENGTH</u>	<u>CONTENTS</u>	<u>FORMAT</u>
1-5	5	'X '	
6-7	2	FORM SUFFIX	
8	1	'H'	
9-16	8	DATE	MM/DD/YY
17-28	12	ICP ID NUMBER	CHARACTER
29-40	12	FLAME AA ID NUMBER	CHARACTER
41-52	12	FURNACE AA ID NUMBER	CHARACTER

INSTRUMENT DETECTION LIMITS (QUARTERLY) DETAIL RECORDS:

<u>COLUMN(S)</u>	<u>LENGTH</u>	<u>CONTENTS</u>	<u>FORMAT</u>
1-5	5	'X '	
6-7	2	FORM SUFFIX	
8	1	'D'	
9-10	2	ANALYTE SYMBOL	CHARACTER
11-17	7	WAVELENGTH	NUMERIC 4.2
18-19	2	BACKGROUND	'BS'/'BD'/'BZ'/BLANK
20-27	8	IDL	NUMERIC 6.1
28-29	2	METHOD (M)	METHOD CODE/'NR'

FORM XI (PART 1)

ICP INTERELEMENT CORRECTION FACTORS (ANNUALLY) HEADER RECORD:

<u>COLUMN(S)</u>	<u>LENGTH</u>	<u>CONTENTS</u>	<u>FORMAT</u>
1-5	5	'XI '	
6-7	2	FORM SUFFIX	AA
8	1	'H'	
9-20	12	ICP ID NUMBER	CHARACTER
21-28	8	DATE	MM/DD/YY

ICP INTERELEMENT CORRECTION FACTORS (ANNUALLY) DETAIL RECORDS:

<u>COLUMN(S)</u>	<u>LENGTH</u>	<u>CONTENTS</u>	<u>FORMAT</u>
1-5	5	'XI '	
6-7	2	FORM SUFFIX	
8	1	'D'	
9-10	2	ANALYTE SYMBOL	CHARACTER
11-17	7	WAVELENGTH	NUMERIC 4.2
18-19	2	ELEMENT 1 SYMBOL	AL
20-29	10	ELEMENT 1 FACTOR	NUMERIC S1.7
30-31	2	ELEMENT 2 SYMBOL	CA
32-41	10	ELEMENT 2 FACTOR	NUMERIC S1.7
42-43	2	ELEMENT 3 SYMBOL	FE
44-53	10	ELEMENT 3 FACTOR	NUMERIC S1.7
54-55	2	ELEMENT 4 SYMBOL	MG
56-65	10	ELEMENT 4 FACTOR	NUMERIC S1.7
66-67	2	ELEMENT 5 SYMBOL	CHARACTER
68-77	10	ELEMENT 5 FACTOR	NUMERIC S1.7

NOTE: FORM XII (Part 1) can only have a FORM SUFFIX of AA. In addition, ELEMENTs 1, 2, 3 and 4 SYMBOL can only be AL, CA, FE and MG respectively. ELEMENT 5 Symbol can be any other analyte symbol.

FORM XI (PART 2)

ICP INTERELEMENT CORRECTION FACTORS (ANNUALLY) HEADER RECORD:

<u>COLUMN(S)</u>	<u>LENGTH</u>	<u>CONTENTS</u>	<u>FORMAT</u>
1-5	5	'XI '	
6-7	2	FORM SUFFIX	AB, AC, etc
8	1	'H'	
9-20	12	ICP ID NUMBER	CHARACTER
21-28	8	DATE	MM/DD/YY

ICP INTERELEMENT CORRECTION FACTORS (ANNUALLY) DETAIL RECORDS:

<u>COLUMN(S)</u>	<u>LENGTH</u>	<u>CONTENTS</u>	<u>FORMAT</u>
1-5	5	'XI '	
6-7	2	FORM SUFFIX	
8	1	'D'	
9-10	2	ANALYTE SYMBOL	CHARACTER
11-17	7	WAVELENGTH	NUMERIC 4.2
18-19	2	ELEMENT 1 SYMBOL	CHARACTER
20-29	10	ELEMENT 1 FACTOR	NUMERIC S1.7
30-31	2	ELEMENT 2 SYMBOL	CHARACTER
32-41	10	ELEMENT 2 FACTOR	NUMERIC S1.7
42-43	2	ELEMENT 3 SYMBOL	CHARACTER
44-53	10	ELEMENT 3 FACTOR	NUMERIC S1.7
54-55	2	ELEMENT 4 SYMBOL	CHARACTER
56-65	10	ELEMENT 4 FACTOR	NUMERIC S1.7
66-67	2	ELEMENT 5 SYMBOL	CHARACTER
68-77	10	ELEMENT 5 FACTOR	NUMERIC S1.7

NOTE: The first FORM XII (Part 2) must have a FORM SUFFIX of AB, the second must have a FORM SUFFIX of AC and so on.

FORM XII

ICP LINEAR RANGES (QUARTERLY) HEADER RECORD:

<u>COLUMN(S)</u>	<u>LENGTH</u>	<u>CONTENTS</u>	<u>FORMAT</u>
1-5	5	'XII '	
6-7	2	FORM SUFFIX	
8	1	'H'	
9-20	12	ICP ID NUMBER	CHARACTER
21-28	8	DATE	MM/DD/YY

ICP LINEAR RANGES (QUARTERLY) DETAIL RECORDS:

<u>COLUMN(S)</u>	<u>LENGTH</u>	<u>CONTENTS</u>	<u>FORMAT</u>
1-5	5	'XII '	
6-7	2	FORM SUFFIX	
8	1	'D'	
9-10	2	ANALYTE SYMBOL	CHARACTER
11-16	6	INTEGRATION TIME	NUMERIC 3.2 (SECONDS)
17-27	11	CONCENTRATION	NUMERIC 9.1
28-29	2	METHOD (M) (ICP IS ASSUMED IF BLANK)	'NR'/BLANK

FORM XIII

PREPARATION LOG HEADER RECORD:

<u>COLUMN(S)</u>	<u>LENGTH</u>	<u>CONTENTS</u>	<u>FORMAT</u>
1-5	5	'XIII '	
6-7	2	FORM SUFFIX	
8	1	'H'	
9-10	2	METHOD	METHOD CODE

PREPARATION LOG DETAIL RECORDS:

<u>COLUMN(S)</u>	<u>LENGTH</u>	<u>CONTENTS</u>	<u>FORMAT</u>
1-5	5	'XIII '	
6-7	2	FORM SUFFIX	
8	1	'D'	
9-15	7	EPA SAMPLE NUMBER	CHARACTER
16-23	8	PREP DATE	MM/DD/YY
24-28	5	WEIGHT	NUMERIC 2.2
29-32	4	VOLUME	NUMERIC 4

FORM XIV

ANALYSIS RUN LOG HEADER RECORD:

<u>COLUMN(S)</u>	<u>LENGTH</u>	<u>CONTENTS</u>	<u>FORMAT</u>
1-5	5	'XIV '	
6-7	2	FORM SUFFIX	
8	1	'H'	
9-20	12	INSTRUMENT ID NUMBER	CHARACTER
21-22	2	METHOD	METHOD CODE
23-30	8	START DATE	MM/DD/YY
31-38	8	END DATE	MM/DD/YY

ANALYSIS RUN LOG DETAIL RECORDS:

<u>COLUMN(S)</u>	<u>LENGTH</u>	<u>CONTENTS</u>	<u>FORMAT</u>
1-5	5	'XIV '	
6-7	2	FORM SUFFIX	
8	1	'D'	
9-16	8	EPA SAMPLE NUMBER	CHARACTER
17-24	8	DILUTION FACTOR	NUMERIC 5.2
25-28	4	TIME	HHMM
29-35	7	PERCENT RECOVERED	NUMERIC S4.1
36	1	ANALYTE (AL)	"X"/BLANK
37	1	ANALYTE (SB)	"X"/BLANK
38	1	ANALYTE (AS)	"X"/BLANK
39	1	ANALYTE (BA)	"X"/BLANK
40	1	ANALYTE (BE)	"X"/BLANK
41	1	ANALYTE (CD)	"X"/BLANK
42	1	ANALYTE (CA)	"X"/BLANK
43	1	ANALYTE (CR)	"X"/BLANK
44	1	ANALYTE (CO)	"X"/BLANK
45	1	ANALYTE (CU)	"X"/BLANK
46	1	ANALYTE (FE)	"X"/BLANK
47	1	ANALYTE (PB)	"X"/BLANK
48	1	ANALYTE (MG)	"X"/BLANK
49	1	ANALYTE (MN)	"X"/BLANK
50	1	ANALYTE (HG)	"X"/BLANK
51	1	ANALYTE (NI)	"X"/BLANK
52	1	ANALYTE (K)	"X"/BLANK
53	1	ANALYTE (SE)	"X"/BLANK
54	1	ANALYTE (AG)	"X"/BLANK
55	1	ANALYTE (NA)	"X"/BLANK
56	1	ANALYTE (TL)	"X"/BLANK
57	1	ANALYTE (V)	"X"/BLANK
58	1	ANALYTE (ZN)	"X"/BLANK
59	1	ANALYTE (CN)	"X"/BLANK

COMMENT RECORDS

COMMENT records are optional for any FORM ID/FORM SUFFIX group. There may be up to 4 COMMENT records per group. They must come after the DETAIL records and be formatted as follows:

<u>COLUMN(S)</u>	<u>LENGTH</u>	<u>CONTENTS</u>	<u>FORMAT</u>
1-5	5	FORM ID	
6-7	2	FORM SUFFIX	
8	1	'C'	
9-78	70	COMMENTS	FREE FORM TEXT

The text may be in paragraph form if desired, but must be contained in columns 9 through 78 only. The key fields must be repeated in columns 1 through 8 of each line.

SECTION III

FORMAT B SPECIFICATION

1. Introduction

1.1 This constitutes the implementation of the EPA standard for media and record formats to be used in transmission of analytical results for the CLP inorganics program. The following points should be noted:

1.1.1 Spaces between fields permit these records to be prepared by programs written for laboratory automation systems in versions of BASIC which require this feature, as well as to be compatible with Agency standard statistical and database management systems (e.g. SAS, S2K, ADABAS, etc.).

1.1.2 Record formats contain sequence numbers and checksums to be consistent with requirements for a future error-free telecommunications format.

2. Record Types

2.1 There are four groups of record types in the reporting format, as shown below. Detailed record formats follow.

<u>Type</u>	<u>Name</u>	<u>Contents</u>
10	Run Header	Contains information pertinent to the whole production run. See production run definition below.
20	Sample Header	Contains sample-identifying information, or corresponding information for calibrations, QC samples, instrument performance checks, etc.
30	Results Record	Contains any final result on a sample, calibration or QC sample and identifying information.
90	Comments Record	Contains free-form comments and/or other miscellaneous information.

2.2 All record types given are mandatory. Type 20, representing the sample, contains the EPA Sample ID which acts as an identifying label for the sample. The QC code indicates whether the data is from an environmental sample, calibration, or QC sample; or other calculated run-wide data such as instrument detection limits or interelement correction factors (if determined using a separate injection). Type 30, representing an individual analyte, contains an identifier to identify the analyte. All 30 series records following that record pertain to the same analyte. See section 11 for an example of the sequence of record types.

3. Production Runs

A production run represents a "group" or "batch" of samples that are processed in a continuous sequence under relatively stable conditions. Specifically:

Calibration - All samples in a run use the same initial calibration data.

Method number - Constant.

Instrument conditions - Constant throughout a run. Results obtained on different instruments cannot be combined in one run.

Thus, each separate group of analyses on each instrument will consist of a separate production run, and be reported in a separate file.

4. Record Sequence (See section 11)

4.1 A Run Header (type 10) record must be present as the first record in the file. Further occurrences of the type 10 record in the file are not allowed.

4.2 Each environmental sample, calibration, or quality control sample is represented by a group composed of a type 20 and 21 records, which holds sample level identifying information, followed by one type 30 record for each analyte. The type 20 record holds a count for the number of analytes being determined. Type 20 records should occur in the order of sample analysis. The type 20 records for quality control items have the additional rule that the LD1 record must occur before the corresponding LD2 record, but the records need not be adjacent. In addition, a type 20 record is used as a header for any additional run-wide data that must be reported for each analyte (such as instrument detection limits). Unique identifiers given in section 9.4 are used in place of "QC codes" to indicate the type of data that follows. Type 30 records for each compound must occur in the order specified on Form 5.

4.3 Type 90 comment records may be defined to occupy any position except before the type 10 (header) record.

5. File/Record Integrity

All record types must contain the following check fields to ensure file and record integrity:

<u>Record Position</u>	<u>Field Length</u>	<u>Field Contents</u>	<u>Remarks</u>
1-2	2	Record type or identifier	"10" or as appropriate
72-74	3	Record sequence number within file	000-999, repeated as necessary
75-78	4	Record checksum	Four hexadecimal digits*; Calculation algorithm to be supplied
79-80	2	Contains CR and LF	

6. Dates and Times

Wherever a date or time-of-day is required, the information consists of successive groups of two decimal digits each, separated by blanks. Dates are given in the order YY MM DD, and times as HH MM. All hours will be given as 0 to 23 using a 24 hour clock and will be local time. Since some computers generating the date and time sequence may have difficulty producing leading zeros, these will not be required.

7. Multiple Volume Data

There is no requirement under this format that all the data from an entire sample delivery group fit onto a single diskette. If a single production run is being split onto multiple diskettes, then it is necessary that all files start with a type 10 record, and that the multiple type 10 records for each file of the same production run be identical. If it is necessary to split the data from a single sample onto multiple diskettes, then the type 20 and following type records for that sample must be repeated. In this situation, it is mandatory that columns 7-33, which collectively identify the sample, be identical in each diskette.

* The checksum is defined to be the sum of the thirty-five (35) INTEGERS that make up the data in columns 1 to 70 when the data is represented in the format 35A2 on processors which store the data bytes in left to right order. The sum is taken modulo 65536 (2^{16}) and represented as four (4) hexadecimal digits. For processors which use an A70 character representation of the data, the checksum is the sum of all the even character position values plus 256 times the sum of all odd character position values.

8. Record Listing

8.1 Format of the mandatory Production Run Header Record (Type 10)

<u>Record Position</u>	<u>Field Length</u>	<u>Field Contents</u>	<u>Remarks</u>
1-2	2	Record type	"10"
3-18	16	blank	
19-21	3	Measurement Type	"ICP", "AA ", or "CN "
22-26	5	blank	
27-30	4	Method Number	Standard method number. See
31	1	blank	sections 9 and 10 for examples
32-34	3	Person responsible for run	3 initials of Manager.
35	1	blank	
36-41	6	Lab ID	From EPA standard list or
42	1	blank	Project Officer
43-50	8	Date Report Prepared	YY MM DD
51	1	blank	
52-61	10	Contract Number	Agency standard number
62	1	blank	
63-68	6	Instrument ID	e.g. AA8312; provided by contract lab; left justi- fied; must be unique and permanent within lab

8.2 Format of the mandatory Sample Header Data Record (Type 20)

<u>Record Position</u>	<u>Field Length</u>	<u>Field Contents</u>	<u>Remarks</u>
1-2	2	Record type	"20"
3-6	4	blank	
7-12	6	EPA Sample No.	Left justified. See below
13-15	3	blank	for calibrations and blanks.
16	1	Sample Medium/Matrix Code	See paragraph 9.3
17	1	blank	
18-20	3	QC code	Codes type of data to be
21	1	blank	reported; (see section 9)
22-24	3	Sample Qualifier	Code to qualify the results
25	1	blank	of the entire sample
			analysis (see paragraph 9.4.1)
26-30	5	Case number	
31-39	9	blank	
40-47	8	Date of Instrumental Anal.	YY MM DD
48	1	blank	
49-53	5	Hour, Minute of Analysis	HH MM
54-67	14	blank	
68-70	3	Analyte Count	Numeric; 1-3 decimal digits;
			right justified - gives the
			number of analytes determined
			by this method for this
			sample.

For unknown samples, use the assigned EPA Sample No. Label standards and blanks as follows:—

INITIAL CALIBRATION (Form 2A)	ICV
CONTINUING CALIBRATION (Form 2A)	CCV1, CCV2, etc.
AA CRDL STANDARD (Form 2B)	CRA
ICP INITIAL LRA STANDARD (Form 2B)	CRII
ICP FINAL LRA STANDARD (Form 2B)	CRIF
INITIAL CALIBRATION BLANK (Form 3)	ICB
CONTINUING CALIBRATION BLANK (Form 3)	CCB1, CCB2, etc.
PREPARATION BLANK (Form 3)	PB1, PB2
LABORATORY CONTROL SAMPLE (Form 7)	LCS
ICP INITIAL INTERFERENCE CHECK SOLUTION A (Form 4)	ICSAI
ICP INITIAL INTERFERENCE CHECK SOLUTION AB (Form 4)	ICSABI
ICP FINAL INTERFERENCE CHECK SOLUTION A (Form 4)	ICSAF
ICP FINAL INTERFERENCE CHECK SOLUTION AB (Form 4)	ICSABF

8.3 Format of the Sample Header Data Record (Type 21)

Use: Continuation of type 20.

Position: Follows the type 20 to which it applies.

<u>Record Position</u>	<u>Field Length</u>	<u>Field Contents</u>	<u>Remarks</u>
1-2	2	Record type	"21"
3	1	blank	
4	1	Method Variation Code (N)	Codes Flame, Furnace, ICP. See section 10
5	1	blank	
6	1	Concentration level	"L" = low "M" = medium (See note)
7-17	11	blank	
18-23	6	SAS Number	Alphanumeric; left justified
24	1	blank	
25-35	11	Laboratory Sample I.D.	Left justified
36	1	blank	
37-44	8	Date of Beginning of Sample Prep or Preparation of Calibration Solution	YY MM DD
45-47	3	blank	
48-55	8	Date Sample Received at Lab	YY MM DD
56	1	blank	
57-63	7	Source of Analyte (if not unknown sample)	Left justified; company or EPA, that analyte was obtained from (Abbreviated if necessary).

NOTE: The concentration level is an estimate of overall level for all analytes.

8.4 Format of the Sample Conditions Record (Type 22)

Use: Continuation of type 20. Used to describe additional sample conditions.

Position: Follows the type 20 and 21 to which it applies.

<u>Record Position</u>	<u>Field Length</u>	<u>Field Contents</u>	<u>Remarks</u>
1-2	2	Record type	"22"
3-41	39	blank	
42-46	5	Volume in ml	e.g. 1.0 or 0.050
47	1	blank	
48-54	7	Dilution Factor	Right justified; e.g. .001
55-64	10	blank	
65-70	6	Percent Solids	Right justified

8.5 Format of the Associated Injection and Counter Record (Type 23)

Use: Continuation of type 20. Used to describe holding time.

Position: Follows the type 20 and 21 to which it applies.

<u>Record Position</u>	<u>Field Length</u>	<u>Field Contents</u>	<u>Remarks</u>
1-2	2	Record type	"23"
3-61	59	blank	
62	1	"H"	Identifies holding time in days (as on Form 10).
63	1	blank	
64-65	2	Holding Time	In days - only necessary for Hg and CN.

8.6 Format of the Results Data Record (Type 30)

<u>Record Position</u>	<u>Field Length</u>	<u>Field Contents</u>	<u>Remarks</u>
1-2	2	Record type	"30"
3	1	blank	
4	1	"I"	
5-10	6	blank	
11-14	4	Identifier Code	The Method Code (see section 10) for the specific analyte.
15-25	11	blank	
26-30	5	Units of measure	(Left justified) "MG/KG" for solids; "UG/L " for water; "PERCT" for percent
31	1	blank	
32-34	3	Non-numeric result	See paragraph 9.4.2 also called a result qualifier
35	1	blank	
36-41	6	Numeric analytical result	Right justified; fixed point or scientific notation
42	1	blank or 'E'	Blank field will be interpreted as "+00"
43-45	3	Exponent	
46	1	blank	
47	1	Calculated Value Descriptor	Describes following value (See paragraph 9.5)
48	1	blank	
49-54	6	Related Calculated Value	Value represents amount added or other calculated or theoretical value. Format same as 36-46.
55	1	blank or 'E'	
56-58	3	Exponent	
59	1	blank	
60	1	Limit or QC Value Descriptor	Describes following value (See paragraph 9.6)
61	1	blank	
62-66	5	Related or QC Limit Value	Value of item described above.
67	1	blank or 'E'	
68-70	3	Exponent	

8.7 Format of the Instrumental Data Readout Record (Type 31)

Use: To describe an added concentration and a measured absorbance or concentration value. Used to report data for Method of Standard Additions (Form 8).

Position: Follows type 30.

<u>Record Position</u>	<u>Field Length</u>	<u>Field Contents</u>	<u>Remarks</u>
1-2	2	Record type	"31"
3	1	blank	
4	1	"C"	Indicates Concentration in ug/L
5	1	blank	
6	1	"B" or "C"	Indicates Absorbance (B) or Concentration (C).
7	1	blank	
8	1	Sequence Number	"0" to "3"
9	1	blank	
10-17	8	Concentration Added	(right justified)
18	1	blank	
19-28	10	Absorbance/Concentration Value	up to 10 decimal digits, right justified

8.8 Format of the Auxiliary Data Record (Type 32)

Use: To report wavelength values used for instrument detection limit determinations and integration times for linear range data.

Position: Follows type 30. (Record will only be required for IDLs and LVMs)

<u>Record Position</u>	<u>Field Length</u>	<u>Field Contents</u>	<u>Remarks</u>
1-2	2	Record type	"32"
3-8	6	blank	
9-10	2	"IT" or "IW"	Indicates Integration time (IT) or IDL wavelength (IW)
11	1	blank	
12-21	10	Wavelength or Time Value	Fixed or Scientific notation as in Record Type 30.

8.9 Format of the Correction Data Record (Type 35)

Use: To record ICP interelement correction factor data.

Position: Follows type 30.

<u>Record Position</u>	<u>Field Length</u>	<u>Field Contents</u>	<u>Remarks</u>
1-2	2	Record Type	"35"
3	1	blank	
4-6	3	"ICP"	Indicates ICP interelement correction factors
7-13	7	blank	
14-21	8	Date factor was determined	YY MM DD
22-27	6	blank	
28-31	4	Identifier of interfering element	from Section 10
32	1	blank	
33-40	8	Wavelength value	
41	1	blank	
42-51	10	Correction factor	Use space as in result field on type 30; fixed or scientific notation

8.10 Format of the Comment Record (Type 90)

Use: To provide for Operator Entered Comments

Position: May occur anywhere.

<u>Record Position</u>	<u>Field Length</u>	<u>Field Contents</u>	<u>Remarks</u>
1-2	2	Record Type	"90"
3	1	blank	
4-70	67	Any Comment	

8.11 Format of the Flags Record (Type 91)

Use: To provide for multiple Form 1 Result Qualifier Flags

Position: Immediately follows the type 30 record to which it applies.

<u>Record Position</u>	<u>Field Length</u>	<u>Field Contents</u>	<u>Remarks</u>
1-2	2	Record Type	"91"
3	1	blank	
4-6	3	Second Result Qualifier Flag	See paragraph 9.4.2 for definitions
7	1	blank	
8-10	3	Third Result Qualifier Flag	
11	1	blank	
12-14	3	Fourth Result Qualifier Flag	
15	1	blank	
16-18	3	Fifth Result Qualifier Flag	
19	1	blank	
20-22	3	Sixth Result Qualifier Flag	
23	1	blank	
24-26	3	Seventh Result Qualifier Flag	
27	1	blank	
28-30	3	Eighth Result Qualifier Flag	

8.12 Format of the Auxiliary Sample Record (Type 92)

Second Use: To provide additional Sample Descriptive Information.

Position: Follows the type 20(-23) record(s) to which it applies.

<u>Record Position</u>	<u>Field Length</u>	<u>Field Contents</u>	<u>Remarks</u>
1-2	2	Record Type	"92"
3	1	blank	
4-17	14	Lab Sample ID	Use entries from Form 1 for each sample.
18	1	blank	
19-28	10	Color Before	
29	1	blank	
30-39	10	Color After	
40	1	blank	
41-46	6	Clarity Before	
47	1	blank	
48-53	6	Clarity After	
54	1	blank	
55-60	6	Texture	
61	1	blank	
62-67	6	Artifacts	

9. Definition of Various Codes Used in Format B Records

9.1 Structure of the Method Number and Identifier Code

The method number and identifier code is a four character alphanumeric code which has the form: XXXY

Where: XXX defines one or more target analytes plus the analytical method. This part of the code is identical with the method numbers defined in EPA methods manuals and the code of Federal Regulations. See section 10.

Y is an alphanumeric modifier which specifies that an allowed option in the method has been implemented, or specifies fractions of analytes in the method. For example, Y may distinguish total and dissolved phosphorous measured by the same method, but with or without the optional method filtration. Another use of Y is to label results which have been determined by the Method of Standard Additions.

If Y is not defined in a method, the default value is one.

The method number is validated as alphanumeric for XXX and Y. It is stored in the four (4) digit number field. Identifier codes are used to identify each metal in a run consisting of more than one metal analysis. It is the same as the method code for a single specific metal.

See section 10 for examples.

9.2 Definition of Various Codes Used

9.2.1 Quality Control and Related Codes (QCC) in Type 20 Records

NOTE: These QCC appear in the QC code fields of type 20 records. They are used to indicate the type of data that are being reported. See section 8.7.

<u>QCC</u>	<u>Name</u>	<u>Definition</u>
LD1	LABORATORY DUPLICATE FIRST MEMBER	The "Sample (S)" from Form 6.
LD2	LABORATORY DUPLICATE SECOND MEMBER	The "Duplicate (D)" from Form 6.

LCB	LABORATORY CALIBRATION BLANK	The Calibration Blank from Form 3.
LRB	LABORATORY (REAGENT) BLANK	The Preparation Blank from Form 3.

<u>QCC</u>	<u>Name</u>	<u>Definition</u>
LCM	LABORATORY CONTROL SOLUTION	The Laboratory Control Sample from Form 7.
LVM	LABORATORY CALIBRATION CRDL VERIFICATION SOLUTION	The samples used for calibration verification, standards, and LRA determinations on Form 2.
LIM	LABORATORY INTERFERENCE CHECK SOLUTION	The ICP interference check sample from Form 4.

LSO	LABORATORY SPIKED SAMPLE BACKGROUND (ORIGINAL) VALUES	The original sample [reported as Sample Result (SR)] from Form 5.
LSF	LABORATORY SPIKED SAMPLE - FINAL VALUES	The spiked sample [reported as Spiked Sample Result (SSR)] from Form 5.

LDO	LABORATORY DILUTED SAMPLE BACKGROUND (ORIGINAL) VALUES	The original sample [reported as Initial Sample Concentration (I)] from Form 9.
LDF	LABORATORY DILUTED SAMPLE - FINAL VALUES	The diluted sample [reported as Serial Dilution Result (S)] from Form 9.

LDX	LABORATORY DOUBLE PURPOSE PRECISION AND ACCURACY SAMPLE	An environmental sample which is used for both the LSO (background level before spike) and LD1 (first member of a duplicate).

IDL	INSTRUMENT DETECTION LIMIT SOLUTION	The solutions used for instrument detection limits as reported on Form 11.

blank		Unknown sample, not associated with any quality control item.

The following QCC values do not refer to actual samples or calibrations for which laboratory results are obtained. Instead they are used on type 20 records which act as a header, and indicate that additional (usually calculated) analyte specific data will be present on type 30 (and following type) records. Usually this data will apply to an entire production run, in which case it will appear immediately following the type 10 record. If the data applies to only a portion of the samples in the run, it should be placed immediately preceding the samples to which it applies. Much of the rest of the information in the type 20 record may be blank, indicating that this data does not apply to these results.

<u>QCC</u>	<u>Name</u>	<u>Definition</u>
SID	SAMPLE INDEPENDENT (i.e. INSTRUMENT) DETECTION LIMITS	The data following represents sample independent detection limits for each compound as reported on Form 11.
ICF	INTER-ELEMENT CORRECTION FACTORS	The data following represents ICP interelement correction factor measurements for each compound as reported on Form 12.
SDR	SPIKE/DUPLICATE CALCULATED RESULTS	The data following represents calculated QC results for the QC samples LD1 and LD2 (percent RSDs), LSO and LSF (percent recoveries), and LDO and LDF (percent D's); or for all AA post digestion spikes. Data consist of percent RSDs, percent recoveries, or percent D's for each analyte as reported on Forms 5, 6, 9 and 14.

9.3 Codes For Sample Medium (Matrix, Source)

<u>Medium</u>	<u>Code</u>
All Media, Don't Know or Don't Care.	0
Water	1
Soil	H
Sludge	I

9.4 List of Samples and Result Qualifiers

Definition: A sample qualifier or a result qualifier (also called a non-numeric result) consists of 3 characters which acts as an indicator of the fact and the reason that the subject analysis (a) did not produce a numeric result or (b) produced a numeric result but it is qualified in some respect relating to the type or validity of the result.

9.4.1 Sample Qualifiers (See paragraph 8.2)

<u>Qualifier</u>	<u>Full Name</u>	<u>Definition</u>
BAC	BACKGROUND CORRECTION	Background correction has been applied to this group of values.
BEF	BEFORE	Labels ICP corrections that were applied before generating raw data; or spiked samples (LSF) that were spiked prior to method-defined digestion (Form 5A).
AFT	AFTER	Labels ICP corrections that were applied after generating raw data; or spiked samples (LSF) that were spiked after method-defined digestion (Form 5B).
POS	POST DIGESTION SPIKE	Labels furnace AA post digestion spike percent recovery data (from Form 14), and also indicates that measured results from the spiked analysis will not be present and the sample results will be reported using QC codes appropriate to non-spiked samples.

9.4.2 Result Qualifiers (See paragraph 8.6)

<u>Qualifier</u>	<u>Full Name</u>	<u>Definition</u>
BDL	BELOW DETECTABLE LIMITS	Indicates analyte was analyzed for but not detected; ignore value (Form 1 "U" Flag).
NAR	NO ANALYSIS RESULT	There is no analysis result required for this subject parameter (Form 1 "NR" Flag).
FQC	FAILED QUALITY CONTROL —	The analysis result is not reliable because control limits were exceeded when the analysis was conducted. Value is estimated. (Form 1 "M", "W", "N", "**", or "+" Flags).
LLS	LESS THAN LOWER STANDARD	The analysis value is less than the contract required detection limit (Form 1 [] value).
EST	ESTIMATED VALUE	Indicates a value estimated or not reported due to presence of interference (Form 1 "E" Flag).
MSP	PERCENT RECOVERY	The following value represents the percent recovery for the spiked sample.
DPD	PERCENT DIFFERENCE	The following value represents the percent difference of the dilution result from the original.
DPR	PERCENT RSD	The following value represents the percent RSD of the duplicate results.

9.5 Calculated Value Descriptors (See paragraph 8.6)

These codes appear in column 47 to identify the value in columns 49-58.

<u>Qualifier</u>	<u>Full Name</u>	<u>Definition</u>
F	AMOUNT ADDED	Identifies the amount of matrix spike analyte added (for QC code "LSF").
T	TRUE VALUE	Indicates the true value for each analyte (for QC codes "LCM", "LVM", and "LIM").

9.6 Limit or QC Value Descriptors (See paragraph 8.6)

These codes appear in column 60 to identify the value in columns 62-70.

<u>Qualifier</u>	<u>Full Name</u>	<u>Definition</u>
U	UNDETECTED	Value is the corrected sample quantitation limit (Form 1 "U" Value).
P	PERCENT RECOVERY	Value is the Percent Recovery for each compound (for QC codes "LCM", "LVM", and "LIM").
C	CORRELATION COEFFICIENT	Value is the correlation coefficient (r) for any result obtained by the Method of Standard Additions (last digit of identifier is "2").
L	CONTROL LIMIT	Value is CRDL value from Form 6 if present (for QC code "SDR").

10. Example Method and Matrix Codes for Inorganic Methods

The codes given below are examples of method number designations for inorganic analyses. In all of these, the Z position refers to the matrix code and should be interpreted with the aid of paragraph 9.3. The generic value of 1, which represents water, type unknown or not specified", is used for water analysis.

Solid samples are represented by two specific codes, with Z values of H (soil) and I (sludge).

Each method code shown occurs in a type 10 record and acts as the header for the appropriate list of compounds.

<u>XXX</u>	<u>Y</u>	<u>N</u>	<u>Z</u>	<u>Definition</u>
200	4	1	1	Generic code for analysis of total metals in water, after method-defined digestion, by atomic absorption, flame.
200	4	2	1	Generic code for analysis of total metals in water, after method-defined digestion, by atomic absorption, furnace.
200	4	7	1	Generic code for analysis of total metals in water, after method-defined digestion, by ICP

For specific matrix codes, replace Z with the specific value for the type of sample (from paragraph 9.3). For Method Identifiers (see section 8.6), replace XXX with value for the analyte. Change Y to 2 if the value was determined by the Method of Standard Additions (Form 1 "S" Flag). Each identifier shown occurs in a type 30 record and identifies the specific compound.

202	Aluminum	242	Magnesium
204	Antimony	243	Manganese
206	Arsenic	249	Nickel
208	Barium	258	Potassium
210	Beryllium	270	Selenium
213	Cadmium	272	Silver
215	Calcium	273	Sodium
218	Chromium	279	Thallium
219	Cobalt	282	Tin
220	Copper	286	Vanadium
236	Iron	289	Zinc
239	Lead		

NOTE: Exception to above:

<u>XXX</u>	<u>Y</u>	<u>N</u>	<u>Z</u>	<u>Definition</u>
245	1	1	1	Analysis of mercury in water by the manual cold vapor technique
245	1	2	1	Analysis of mercury in water by the automated cold vapor technique
<u>XXX</u>	<u>Y</u>	<u>N</u>	<u>Z</u>	<u>Definition</u>
245	4	5	H	Analysis of mercury in soil, after method-defined digestion, by the manual cold vapor technique
245	4	5	I	Analysis of mercury in sludge, after method-defined digestion, by the manual cold vapor technique
335	1	2	1	Analysis of total cyanide in water by titrimetric, manual spectrophotometric, or semi-automated spectrophotometric means

NOTES:

1. See paragraph 9.1 for the structure of "XXX" and "Y"
2. If multiple metals are analyzed as part of a single production run, the method code (paragraph 8.1) is "2004". If only a single metal is analyzed, then use the value for that metal (i.e. "2064" for arsenic). In all cases the identifier in paragraph 8.6 is a specific code given in Section 10.
3. The values of "N" and "Z" are sample dependent and may vary within a production run. They are reported on type 20 and 21 records (paragraphs 8.2 and 8.3)

11. Example of the Sequence of Record Types in a Production Run

10 Contains Run Header information
20 Occurs once for each sample, calibration, calculated QC results,
 instrument detection limits, etc. - Acts as a header.
 21 Will usually be present
 22 Contains additional information for samples
30 Occurs once for each final analytical result. Will give
 whatever value is being determined as defined by the type 20.
 31 Reports any instrumental data necessary
 32 Reports any auxiliary data necessary
 35 Reports corrections to results if necessary
30 Values for the next analyte or parameter being measured.
 31 Additional data may vary for each parameter, and records
 32 may occur in any order. Multiple occurrences of the
 32 same record type, however, must be consecutive.
 35
30 Continues for as many as are necessary
 31
 32
 35
30 31
 32
 35
20 Next Sample Header record - The following applies to the next
 21 sample or other group of data.
 22
30 31
 32
30 31
 32 etc.
20 21
30 31
 32 etc.

12. Format of Records for Specific Purposes

12.1 Format of the Sample Header Data Record (Type 20) for Linear Range Analysis

<u>Record Position</u>	<u>Field Length</u>	<u>Field Contents</u>	<u>Remarks</u>
1-2	2	Record type	"20"
3-6	4	blank	
7-10	4	"LRAI" or "LRAF"	To indicate initial or final
11-15	5	blank	
16	1	"0"	No matrix code
17	1	blank	
18-20	3	"LVM"	See paragraph 9.2
21-25	5	blank	
26-30	5	Case number	
31-66	36	blank	
67-69	3	Analyte Count	Numeric; 1-3 decimal digits; right justified - gives the number of analytes determined by this method for this sample.

12.2 Format of the Sample Header Data Record (Type 21) for Linear Range Analysis

<u>Record Position</u>	<u>Field Length</u>	<u>Field Contents</u>	<u>Remarks</u>
1-2	2	Record type	"21"
3	1	blank	
4	1 -	"7"	Codes ICP. See Section 10
5-17	13	blank	
18-23	6	S A S Number	Alphanumeric; left justified
24-36	13	blank	
37-44	8	Date of Preparation of Calibration Solution	YY MM DD
45-56	12	blank	
57-63	7	Source of Analyte	Left justified; company or EPA, that compound was obtained from (abbreviated if necessary).

12.3 Format of the Results Data Record (Type 30) for Linear Range Analysis

<u>Record Position</u>	<u>Field Length</u>	<u>Field Contents</u>	<u>Remarks</u>
1-2	2	Record type	"30"
3	1	blank	
4	1	"I"	
5-10	6	blank	
11-14	4	Identifier Code	The Method Code (section 10) for the specific compound.
15-25	11	blank	
26-30	5	"UG/L "	Units
31-35	5	blank	
36-41	6	Found Value	Right justified; fixed point or scientific notation.
42	1	blank or 'E'	
43-45	3	Exponent	
46	1	blank	
47	1	"T"	Indicates true value See paragraph 9.5
48	1	blank	
49-54	6	True Value	Format same as 36-46.
55	1	blank or 'E'	
56-58	3	Exponent	
59	1	blank	
60	1	"P"	Indicates percent recovery See paragraph 9.6
61	1	blank	
62-66	5	Percent Recovery	
67	1	blank or 'E'	
68-70	3	Exponent	

12.4 Format of the Auxiliary Data Record (Type 32) for Linear Range Analysis
(only for quarterly submissions)

<u>Record Position</u>	<u>Field Length</u>	<u>Field Contents</u>	<u>Remarks</u>
1-2	2	Record type	"32"
3-8	6	blank	
9-10	2	"IT"	Indicates Integration time
11	1	blank	
12-21	10	Integration Time Value	Fixed or Scientific notation

12.5 Format of the Sample Header Data Record (Type 20) for Duplicate Data

<u>Record Position</u>	<u>Field Length</u>	<u>Field Contents</u>	<u>Remarks</u>
1-2	2	Record type	"20"
3-6	4	blank	
7-12	6	EPA Sample ID	Left justified
13-15	3	blank	
16	1	Sample Medium/Matrix Code	See paragraph 9.3
17	1	blank	
18-20	3	"SDR"	Identifies calculated QC results
21-25	5	blank	
26-30	5	Case number	
31-67	37	blank	
68-70	3	Analyte Count	Numeric; 1-3 decimal digits; right justified - gives the number of analyte determined by this method for this sample.

12.6 Format of the Sample Header Data Record (Type 21) for Duplicate Data

<u>Record Position</u>	<u>Field Length</u>	<u>Field Contents</u>	<u>Remarks</u>
1-2	2	Record type	"21"
3	1	blank	
4	1	Method Variation Code (N)	Codes flame, furnace, ICP. See section 10
5	1	blank	
6	1	Concentration level	"L" = low "M" = medium
7-17	11	blank	
18-23	6	SAS Number	Alphanumeric; left justified
24	1	blank	
25-35	11	Laboratory Sample ID	Left justified

12.7 Format of the Results Data Record (Type 30) for Duplicate Data

<u>Record Position</u>	<u>Field Length</u>	<u>Field Contents</u>	<u>Remarks</u>
1-2	2	Record type	"30"
3	1	blank	
4	1	"I"	
5-10	6	blank	
11-14	4	Identifier Code	The Identifier Code (section 10) for the specific compound.
15-25	11	blank	
26-30	5	"PERCT".	Units are percent
31	1	blank	
32-34	3	"DPR"	Indicates Duplicate %RSD
35	1	blank	
36-41	6	Duplicate Percent RSD	Right justified; fixed point or scientific notation.
42	1	blank or 'E'	
43-45	3	Exponent	

12.8 Format of the Sample Header Data Record (Type 20) for Continuing Checks

<u>Record Position</u>	<u>Field Length</u>	<u>Field Contents</u>	<u>Remarks</u>
1-2	2	Record type	"20"
3-6	4	blank	
7-10	4	"CCV1" "CCV2" etc	To indicate which check
11-15	5	blank	
16	1	"0"	All matrices
17	1	blank	
18-20	3	"LVM"	See paragraph 9.4.1
21-25	5	blank	
26-30	5	Case number	
31-66	36	blank	
67-69	3	Analyte Count	Numeric; 1-3 decimal digits; right justified - gives the number of analytes determined by this method.

12.9 Format of the Sample Header Data Record (Type 21) for Continuing Checks

<u>Record Position</u>	<u>Field Length</u>	<u>Field Contents</u>	<u>Remarks</u>
1-2	2	Record type	"21"
3	1	blank	
4	1	Method Variation Code (N)	Codes Flame, Furnace, ICP.
5-17	13	blank	See Section 10
18-23	6	S A S Number	Alphanumeric; left justified
24-36	13	blank	
37-44	8	Date of Preparation of Calibration Solution	YY MM DD
45-56	12	blank	
57-63	7	Source of Analyte	Left justified; company or EPA, that analyte was obtained from.

NOTE: The Results Data Record (Type 30) for Continuing Checks is identical to that for Linear Range Data. See paragraph 12.3. Record type 32 is not present.

12.10 Format of the Results Data Record (Type 30) for an Unknown Sample when the Method of Standard Additions was used.

<u>Record Position</u>	<u>Field Length</u>	<u>Field Contents</u>	<u>Remarks</u>
1-2	2	Record type	"30"
3	1	blank	
4	1	"I"	
5-10	6	blank	
11-14	4	"2XX2"	See Section 10 "XX" values. Last character is a "2".
15-25	11	blank	
26-30	5	Units of measure	"MG/KG" for solids; "UG/L" for water.
31	1	blank	
32-34	3	Non-numeric result	See paragraph 9.4.2; also called a result qualifier
35	1	blank	
36-41	6	Numeric analytical result	Right justified; fixed point or scientific notation
42	1	blank or 'E'	
43-45	3	Exponent	
46	1	blank	
47	1	Calculated Value Descriptor	Describes following value See paragraph 9.5
48	1	blank	
49-54	6	Related Calculated Value	Format same as 36-46. (Only present if spiked sample)
55	1	blank or 'E'	
56-58	3	Exponent	
59	1	blank	
60	1	"C"	Indicates correlation coefficient.
61	1	blank	
62-66	5	r* value	Give value from Form 8 for each analyte determined.
67	1	blank or 'E'	
68-70	3	Exponent	

NOTE: Following each type 30 record where the Method of Standard Additions was used will be four type 31 records (see paragraph 8.7). Each contains data for one of the four additions.

12.11 Format of the Sample Header Data Record (Type 20) for Post Digestion Spike Data

<u>Record Position</u>	<u>Field Length</u>	<u>Field Contents</u>	<u>Remarks</u>
1-2	2	Record type	"20"
3-6	4	blank	
7-12	6	EPA Sample ID	Left justified
13-15	3	blank	
16	1	Sample Medium/Matrix Code	See section 9.3
17	1	blank	
18-20	3	"SDR"	Identifies calculated QC results
21	1	blank	
22-24	3	"PDS"	Label this as post digestion spike data.
25	1	blank	
26-30	5	Case Number	
31-67	37	blank	
68-70	3	Compound Count	Numeric; 1-3 decimal digits; right justified - gives the number of compounds determined for this sample.

12.10 Format of the Results Data Record (Type 30) for Post Digestion Spike Data

<u>Record Position</u>	<u>Field Length</u>	<u>Field Contents</u>	<u>Remarks</u>
1-2	2	Record type	"30"
3	1	blank	
4	1	"I"	
5-10	6	blank	
11-14	4	Identifier Code	The Identifier Code (see section 10) for the specific compound
15-25	11	blank	
26-30	5	"PERCT"	Units are percent
31	1	blank	
32-34	3	"MSP"	Indicates Percent Recovery
35	1	blank	
36-41	6	Percent Recovery	Right justified; fixed point or scientific notation
42	1	blank or "E"	
43-45	3	Exponent	

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